Petroleomic Depth Profiling of Staten Island Salt Marsh Soil: 2ω Detection FTICR MS Offers a New Solution for the Analysis of Environmental Contaminants

Mary J. Thomas[1,2], Emma Collinge[2], Matthias Witt[3], Diana C. Palacio Lozano[2], Christopher H. Vane[4], Vicky Moss-Hayes[4] and Mark P. Barrow[2*]

1. MAS CDT, Senate House, University of Warwick, Coventry, CV4 7AL, UK

2. Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK

3. Bruker Daltonik GmbH, Bremen, 28359, Germany

4. British Geological Survey, Centre for Environmental Geochemistry, Keyworth, NG12 5GG, UK

*Author to whom correspondence should be addressed

Abstract

Staten Island is located in one of the most densely populated regions of the US: the New York/New Jersey Estuary. Marine and industrial oil spills are commonplace in the area, causing the waterways and adjacent marshes to become polluted with a range of petroleum-related contaminants. Using Rock-Eval pyrolysis, the hydrocarbon impact on a salt marsh was assessed at regular intervals down to 1 m, with several key sampling depths of interest identified for further analysis. Ultrahigh resolution data is obtained by direct infusion atmospheric pressure photoionization (APPI) on a 12 T solariX Fourier transform ion cyclotron resonance mass spectrometer (FTICR MS) allows trends in the compositional profile with depth to be observed, such as changes in the relative hydrocarbon intensity and the relative contributions from oxygen- and sulfur-containing groups. These trends may correlate with the timing of major oil spills and leaks of petroleum and other industrial chemicals into the waterways. The use of GC coupled to a 7 T solariX 2XR FTICR MS equipped with an atmospheric pressure chemical ionization (APCI) ion source offers time resolved and extensive compositional information for the complex environmental samples complementary to that obtained by direct infusion APPI. The compositional profile observed using GC-APCI FTICR MS includes contributions from phosphorous containing groups, which may be indicative of contamination from agrochemicals and the impact of agricultural effluent upon Staten Island soil quality.

Introduction

New York/New Jersey (NY/NJ) Estuary supports one the highest population densities in the United States, consequently the shores of one of its main shipping channels, the Arthur Kill, hosts numerous waste generating industries. The NY/NJ Estuary was ranked among the most chemically contaminated waterways in the United States based on surface sediment concentrations and frequency of accidental chemical discharge events.[1,2] Elevated body burdens of toxic substances including heavy metals, petroleum hydrocarbons, and aromatic hydrocarbons have been detected in a wide range of aquatic wildlife.[1] Analysis of the spatial and down-core extent of contamination by petroleum-related compounds in estuarine and coastal regions is of rising importance due to increased demand on below ground space, which may contain historic pollution, as well as greater understanding of the long term impact on eco-system health.[3-9]

Environmental samples, particularly those contaminated with petroleum-related products, are highly complex, containing many thousands of components.[9,10,11] The characterization of petroleum-related samples using mass spectrometry has been termed 'petroleomics', with the molecular formulae of tens of thousands of components observed in a single spectrum.[12,13] Petroleomics typically utilizes state-of-the-art, high field FTICR instrumentation[14,15] which offers ultrahigh resolution and sub-ppm mass accuracy. However, these instruments are typically expensive to obtain and maintain, as well as requiring expert operation. solariX 2XR FTICR MS instruments can operate in a mode where ion detection occurs using 4 cell plates, compared to the usual 2, and as such are able to detect at twice the usual frequency.[16,17] 2ω detection allows for significant improvements in performance compared to other FTICR instrumentation operating at the same field,[18] specifically doubling resolution for a set acquisition time or else offering equivalent resolution in half the time.[19] The latter makes the technique well suited to hyphenated techniques, including gas chromatography (GC), where a fast scan rate is required to maintain pace with rapidly eluting components.[20-22]

7 T FTICR instrumentation equipped with the option of 2ω detection has already demonstrated ultrahigh resolution analytical capabilities in the analysis of petroleum samples,[16] offering equivalent performance at a lower magnetic field than previously required. This, in turn, reduces the entry cost for FTICR MS for petroleomics and environmental analyses. One of the advantages of the ParaCell in solariX XR and 2XR instruments is the ability to excite ions to a larger orbit radius than the Infinity Cell design, which in turn yields greater signal-to-noise and reduction in space-charge effects.[16] Here, the application is extended to environmental samples, where coupling GC can increase the scope of analysis to include the observation of multiple isomers for a single molecular formula,[23-25] and to provide an additional dimension of separation, aiding in the detection of low abundance species.[25]

Analyses of environmental samples including oil sands process-affected water,[28,29] and soil from coastal regions affected by the Deepwater Horizon spill[30] by direct infusion into FTICR MS instrumentation have been successful. Coupling of chromatographic methods with FTICR MS has also been successfully applied to the characterization of petroleum-contaminated soil[31] and weathered crude oils.[32] The choice of ionization method can influence the observed profile. Atmospheric pressure photoionization (APPI) preferentially accesses non-polar, conjugated systems, and produces both protonated and radical ion species, adding to spectral complexity[14] while atmospheric pressure chemical ionization (APCI) accesses both non-polar and polar compounds.[33] Coupling prior separation techniques, including GC, has been shown to add a further dimension of separation and improve the range of compounds observed by FTICR methods and to provide information on the range of isomers for each unique molecular formula assigned.[34]

In this study, the shallow salt marsh sediment core from Staten Island, New York, was sampled at 47 intervals to correlate the compositional fingerprints of the petroleum extracts with the history of oil spills the area. Rock-Eval(6) pyrolysis, a geochemical screening technique widely applied to the hydrocarbon bearing source rocks, was used as bulk geochemical reconnaissance method.[26,27] Rock-Eval generates parameters for total organic carbon (TOC), free hydrocarbons (S1), and bound (polymeric) hydrocarbons (S2). S1 describes the quantity and proportion of volatile hydrocarbons (free oil) S2 the bound hydrocarbons (biopolymers and kerogen). The production index is used as a benchmark for thermal maturity.

In parallel to Rock–Eval pyrolysis screening geochemistry, solvent extracts were profiled by a combination of direct infusion APPI FTICR MS Fourier transform ion cyclotron resonance mass spectrometry experiments, plus GC-APCI FTICR MS experiments to access additional, low abundance species. The coupling of GC with ultrahigh resolution mass spectrometry affords the ability to accurately monitor signal intensities within very narrow m/z windows; by following the extracted ion chromatograms (EICs) in a manner not possible with lower resolution instrumentation, it is possible to obtain information about the range of isomers for a molecular formula.

The detailed molecular characterization obtained by APPI-FTICR MS (solariX) and GC-APPI FTICR MS (solariX 2XR), along with the bulk information determined by Rock-Eval pyrolysis, allows a fingerprint of the petroleum-based contaminants of the soil to be developed. Petroleomic profiles of soil as a function of depth allow contamination to be correlated with the site history, and aid in understanding of the aging of petroleum-based compounds over time.

Experimental Section

Sediment sampling

A sediment core was collected using a Eijkelkamp peat sampler fitted with a stainless steel gauge (50 cm × 5.2 cm i.d.) at 40 36 27.87912 N, 74 11 27.50687 W (± 5 m) from intertidal zone of Saw Marsh Creek, Staten Island, New York, USA on June 10th 2013 (Figure 1). Recovered core sections were stored in pre-cut clean UPVC pipe and transported in a cool box at approximately 4 °C and then frozen at -18 °C. Each core was sectioned continuously at 2 cm intervals up to and including 46 cm depth and at 1 cm up to 51.5 cm depth and then at 2 cm intervals to core base at 90 cm. All sediment intervals were then freeze-dried for 72 h, sieved through a mesh aperture of 2 mm and the <2 mm fraction ground to a fine powder. [35,36]

Figure 1. Sampling location of Core.

Rock-Eval(6) Pyrolysis

Forty seven depth increments from the Saw Marsh Creek core were analyzed using a Rock-Eval(6) pyrolyser. Powdered samples (60 mg dry wt.) were heated from 300 °C to 650ºC at 25 °C min^{-1} in an inert atmosphere of N_2 and the residual carbon then oxidised at 300 °C to 850 °C at 20 °C min^{-1} (hold 5 min). Hydrocarbons released during the two-stage pyrolysis were measured using a flame ionization detector and CO and CO_2 measured using an IR cell. The performance of the instrument was checked every 10 samples against the accepted values of the Institut Français du Pétrole (IFP) standard (IFP 160 000, S/N1 5-081840). Rock-Eval parameters were calculated by integration of the amounts of HC (thermally-vaporized free hydrocarbons) expressed in mg HC^{-1} g^{-1} rock (S1) and hydrocarbons released from cracking of bound organic matter (OM) expressed in mg HC^{-1} g^{-1} rock (S2). The production index is given by S1/S1+S2.

Soxhlet Extraction

Environmental Protection Agency method 3540c[37] was followed for 5 depth samples. 190 mL dichloromethane (DCM) (Fisher Scientific, Hemel Hempstead, Hertfordshire, UK) was added to each sample and heated at ~40 °C for 22 h. Extracts then cooled before being evaporated under reduced pressure to 10 mL.

Direct Infusion APPI FTICR

Extracts for 5 depths were diluted in dichloromethane (DCM) (Fisher Scientific, Hemel Hempstead, Hertfordshire, UK) before mass spectra were acquired using a 12 T solariX FTICR mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany), coupled to an APPI II source. The instrument was operated in positive-ion mode. Nitrogen was used as the drying gas at a temperature of 200 °C at a flow rate of 4 L min^{-1}. The nebulizing gas was nitrogen and was maintained at a pressure of 1.0 bar. Samples were infused using a syringe pump at a rate of 750 µL h^{-1} without the activation of in-source dissociation. 4 MW data sets were acquired using magnitude mode, with a detection range of m/z 98-3000. After acquiring 300 scans, the data were zero-filled once and apodized using a Sine-Bell function prior to applying a fast Fourier transform. For the apodized data, the measured resolving power at *m/z* 200 was 650,000. Data were internally calibrated using homologous series and analyzed using DataAnalysis 4.2 (Bruker Daltonik GmbH, Bremen, Germany), prior to the data being imported into Composer 1.5.7 (Sierra Analytics, Modesto, CA, USA) for compositional analysis; Aabel NG2 v.5.2 (Gigawiz Ltd. Co., Tulsa, Oklahoma, USA) was used for data visualization.

GC-APCI FTICR

Extracts for 4 depths were diluted in DCM (Sigma Aldrich Chemie GmbH, Munich, Bavaria, Germany). Mass spectra were acquired using a 7 T solariX 2XR FTICR mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany), coupled to a 450 GC and APCI II source. 1 µL injection volume onto a 30 m BR-5ms column was used with He as the carrier gas, with the temperature program as follows: 60 °C held for 1 min, ramping 6 °C min^{-1} up to 300 °C and held for 9 min. The instrument was operated in positive-ion mode. Nitrogen was used as the drying gas at a temperature of 240 °C at a flow rate of 4 L min^{-1}. The nebulizing gas was nitrogen and was maintained at a pressure of 2.0 bar. Samples were infused using a syringe pump at a rate of 2 µL h^{-1} without the activation of in-source dissociation. 2 MW data sets were acquired using magnitude mode, with a detection range of m/z 107-3000 and 95 % data reduction. 2ω detection was used, affording high resolution at the rapid scan rate required for GC-APCI infusion. The data were zero-filled once and apodized using a Sine-Bell function prior to applying a fast Fourier transform. A lock mass of *m/z* 223.06345 (a polysiloxane) was used for calibration. For the apodized data, the measured resolving power at *m/z* 200 was 300,000. Data were analyzed using DataAnalysis 4.2 (Bruker Daltonik GmbH, Bremen, Germany) in 10 minute time retention intervals with the first 10 minutes used for background subtraction, prior to the data being imported into Composer 1.5.7 (Sierra Analytics, Modesto, CA, USA) for compositional analysis; Aabel NG2 v.5.2 (Gigawiz Ltd. Co., Tulsa, Oklahoma, USA) was used for data visualization.

Results and Discussion

Rock-Eval(6)Pyrolysis

Inspection of the TOC content and its two major components, S1 and S2, at each sampling interval (Figure 2) shows a rapid decrease from surface to 25 cm, which may be due to the presence of natural extractable free hydrocarbon compounds and structural biopolymers in the rooting zone of living marsh plants.[38] Below 25 cm depth the hydrocarbon content (TOC, S1, S2) was low and invariant with exception of a broad concentration peak at 47 - 49 cm and another at 79 - 81 cm (Figure 2). These were taken to indicate anthropogenic oil spills, including the possible 1990 Exxon pipeline spill. Similarly corresponding changes were also confirmed by the concentrations of residual carbon (RC %) (non-pyrolyzable) and production index (PI) (Figure 2). The latter parameter is a widely utilized by hydrocarbon explorationists to assess the amount of generated as compared to potential hydrocarbons. In this current work increasing PI values also appear to have considerable utility for the identification of possible hydrocarbon pollution events.

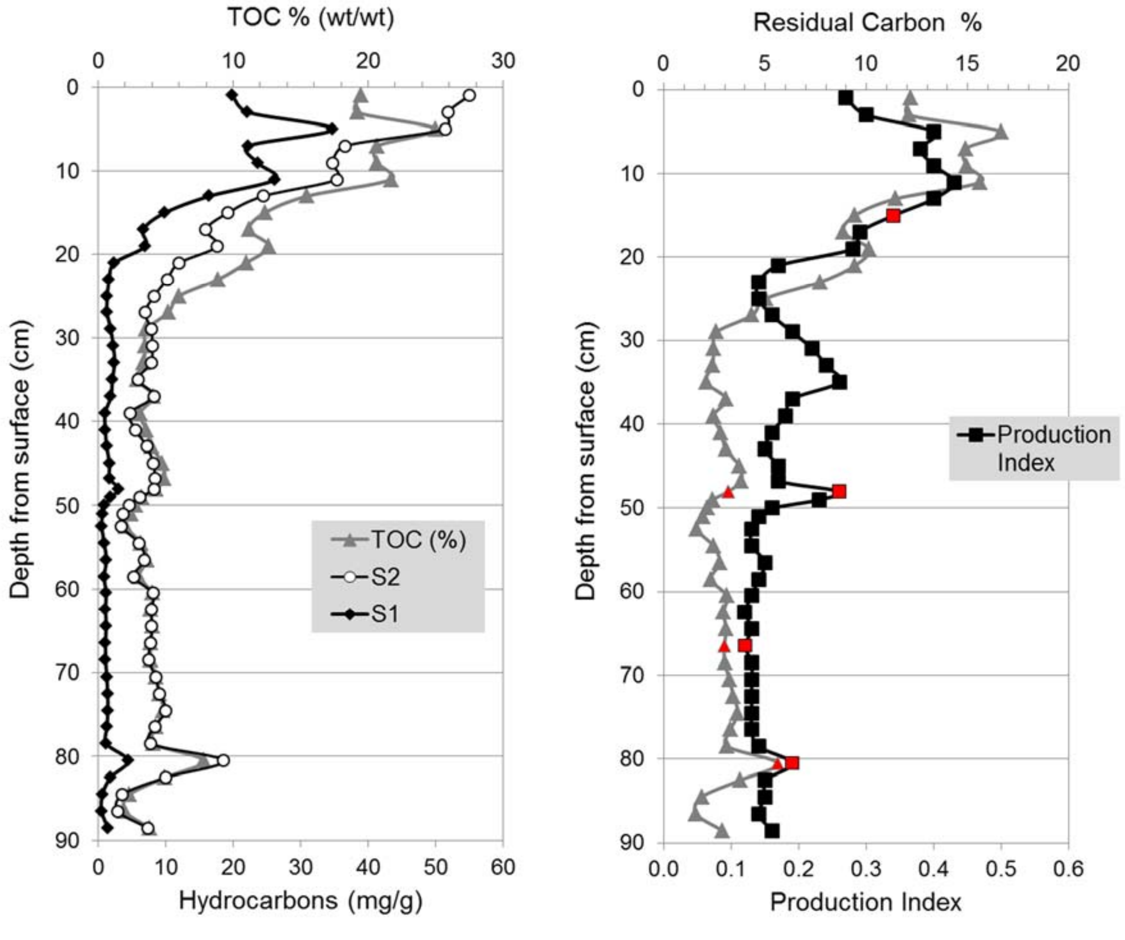

Figure 2. TOC and RC analysis by Rock-Eval(6) Pyrolysis

The key sampling depths carried forward for further analysis by FTICR MS methods are indicated by red markers in Figure 2, with 67.5 – 69.5 cm included as a background sample.

Direct Infusion APPI FTICR MS

Broadband mass spectra were obtained for soil extracts, produced using soil samples originating from 5 depths, with the spectra shown in Figure 3. The mass distribution shifts between extract sampling depths, with 14 - 16 to 67.5 - 69.5 cm centred approximately on *m/z* 350, while 79.5 - 81.5 cm is centred on a higher *m/z* of 500 and has greater spectral intensity over the entire distribution.

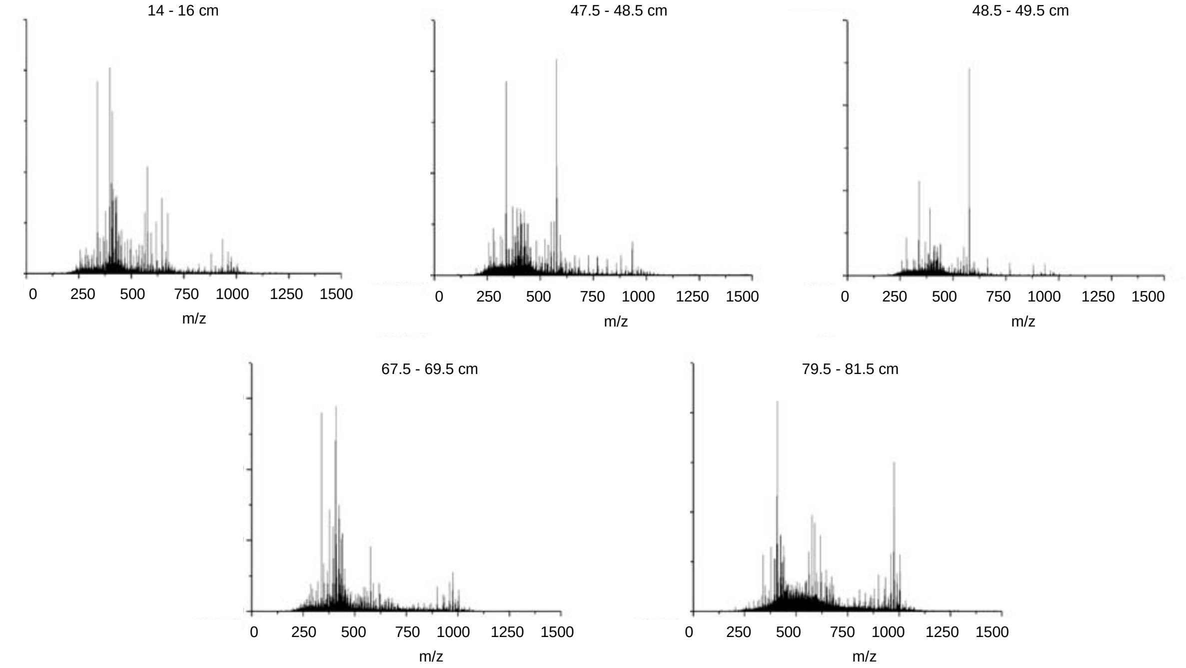

Figure 3. Direct infusion APPI FTICR mass spectra for 5 sampling depths

Direct infusion MS data were analyzed by searching for homologous series of peaks separated by the CH_2 (14.01565 Da) repeat unit. Homologous series of molecular formulae possess the same heteroatom content (compound class) and number of double bond equivalents (DBE)[39], and increase incrementally with each CH_2 repeat unit by one carbon number.[40] A compound class distribution, showing the total relative intensity of peaks assigned to each compound class, is shown for all sampling depths in Figure 4.

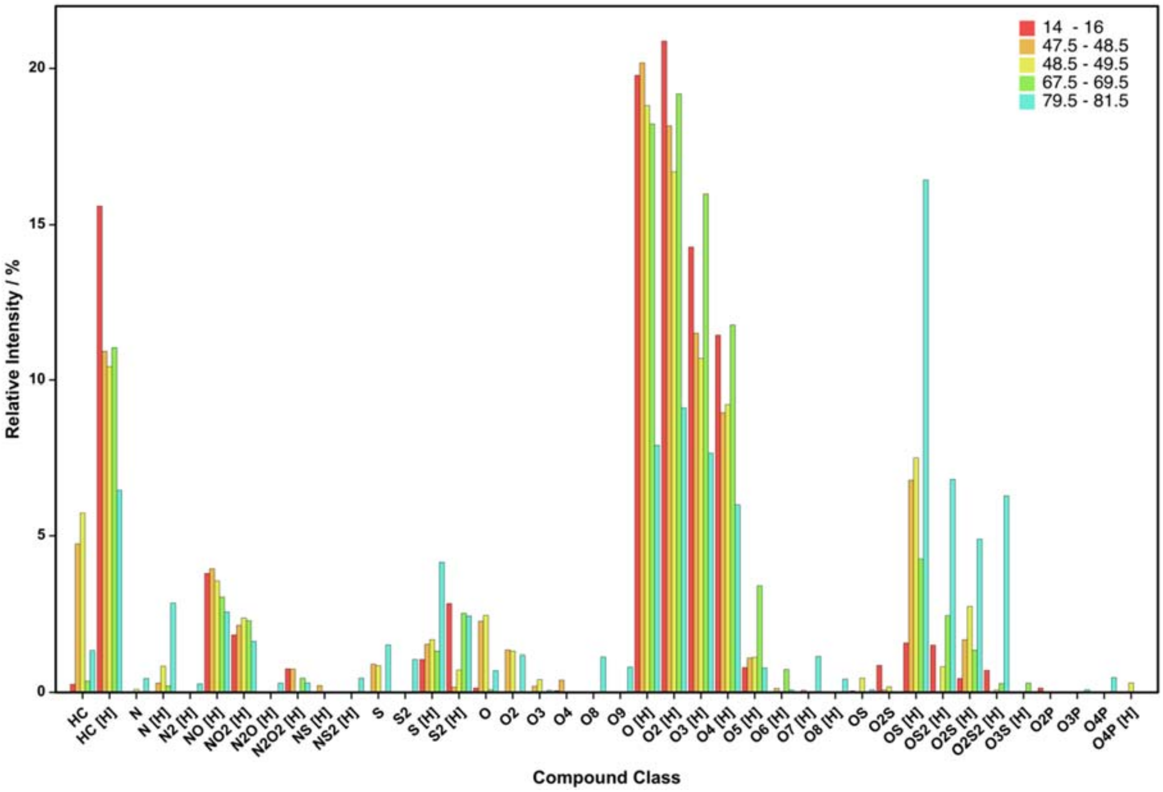

Figure 4. Compound class distribution for 5 sampling depths

Several key compositional differences between sampling depths are seen in Figure 4, particularly a sharp increase in the relative contribution from O_x and O_x[H], and O_xS_y compounds with a high oxygen content, when moving from the shallower samples to the deepest sample at 79.5-81.5 cm. At the depths of 47.5 - 48.5 and 48.5 - 49.5 cm, there is a relatively strong contribution from the HC class, correlating well with the higher concentrations of free and bound hydrocarbons measured by Rock-Eval pyrolysis. The depths of 47.5 - 48.5, 48.5 - 49.5 and 79.5 - 81.5 cm also have contributions from the N[H], S, and O_x classes.

The relative contribution from oxygenated organic compounds was found to increase at the key sampling depths, with corresponding trends in the contributions from sulfur-containing classes also being observed. The increase in contribution from highly oxygenated O_x and O_xS_y classes may be linked to ageing of petroleum compounds,[30,41,42] and may be used to provide information of the timing of contamination due to particular spills.[43]

GC-APCI FTICR MS

The total ion chromatogram (TIC) is shown in Figure 5 for the 67.5 - 69.5 cm depth sample. The average spectra taken over 10 minute time intervals of the TIC, show a shift in petroleum distribution to higher *m/z* with increasing retention time.

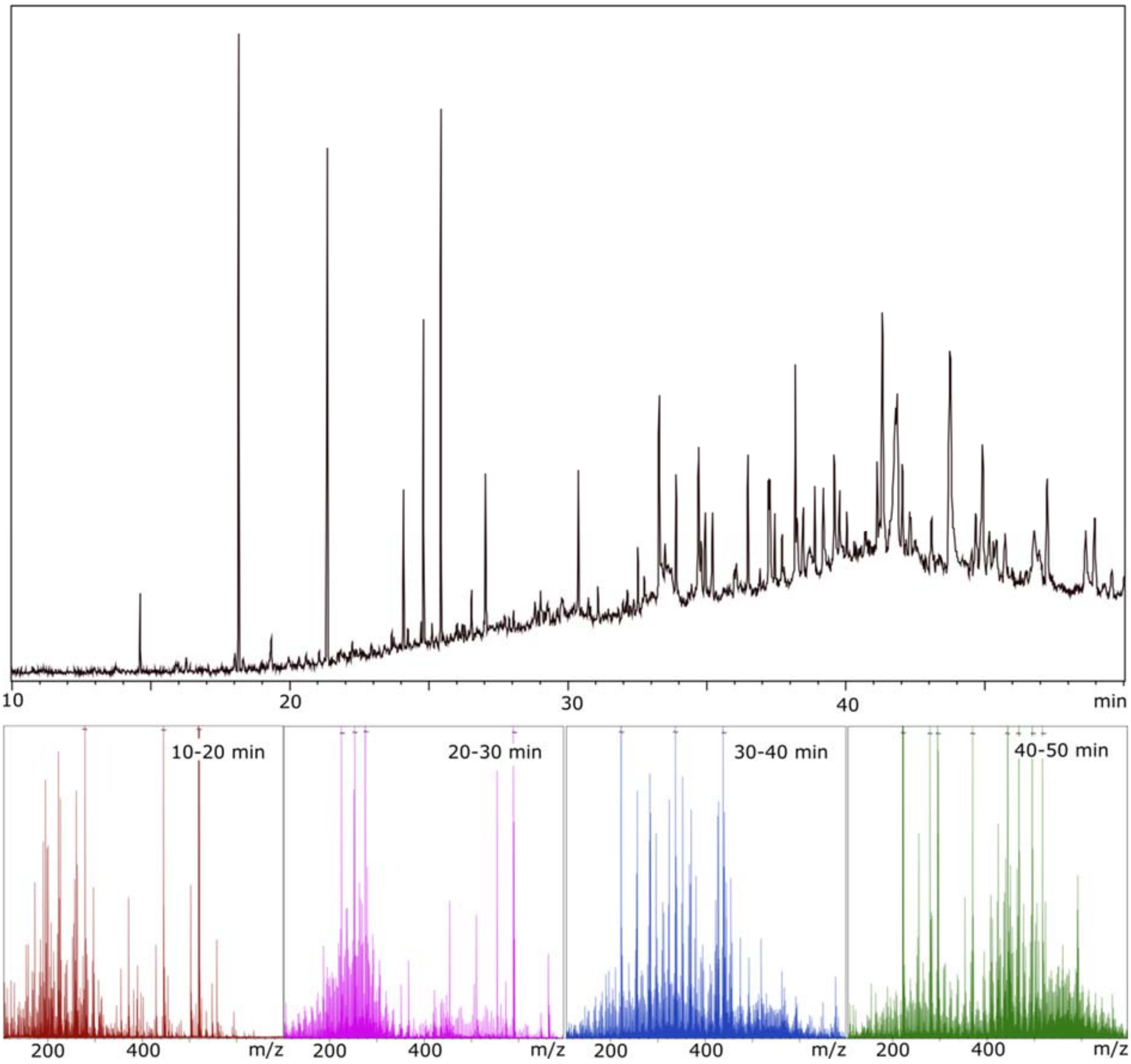

Figure 5. Total ion chromatogram for sampling depth 67.5 – 69.5 cm with the mass spectra resulting from averaging the acquired scans over 10 minute intervals.

Several heteroatom containing compound classes were observed at greater relative intensity when using GC-APCI FTICR MS compared to direct infusion APPI FTICR MS. The compound class analysis shown in Figure 6 for 67.5 - 69.5 cm demonstrates that several classes were more readily observed by GC-APCI FTICR MS experiments compared to direct infusion APPI FTICR MS measurements, including low intensity O_x and O_xP classes. Notably, phosphorous containing classes including $O_4P[H]$ also make a contribution to the depths of 14 – 16 cm and 48.5 – 49.5 cm (SI Figures 1 and 2), typically eluting early in the run. The $O_4P[H]$ class was also detected in the APPI FTICR MS experiments at 48.5 - 49.5 cm. Several possible sources of phosphorous contamination in the NY/NJ Estuary exist, including agricultural effluent, leaks from chemical plants producing agrochemicals including fertilisers, or leaching of materials dumped in the now closed Fresh Kills Landfill.[44] It is of particular note that the sampling depth of 67.5 – 69.5 cm appeared to contain background levels of free volatile hydrocarbons and bound polymeric hydrocarbons, as indicated in Figure 2. Direct infusion APPI and GC-APCI analyses both show that soil at this depth contains a range of petroleum-related compounds as well as other industrial chemicals, which suggests that the NY/NJ Estuary is continually affected by contamination.

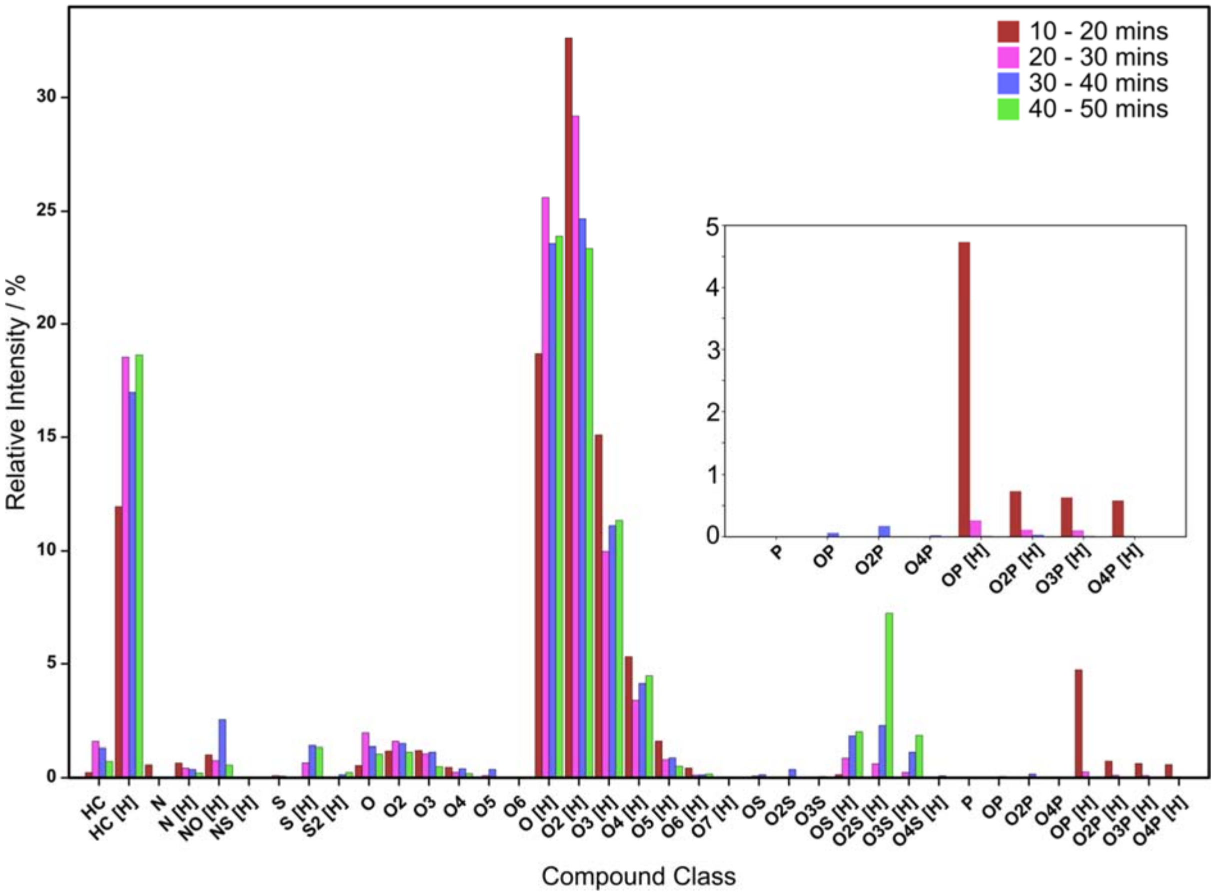

Figure 6. Change in compound class distribution over time from GC-APCI FTICR MS analysis of sampling depth 67.5 – 69.5 cm. An enlarged region showing contributions from the phosphorous containing classes is inset.

Several key components of the soil extract appear to elute preferentially at specific times, most notably the relative contributions from the O_xS[H] classes increase with retention time. NO[H] and S[H] have the greatest relative intensity at 30 - 40 min. The O_xP[H] classes have the greatest relative intensity at the early elution times of 10 - 20 and 20 - 30 min.

Each compound class can be broken down further into a plot of carbon number against number of rings and double bonds, or double bond equivalents (DBE), for each constituent. Figure 6 shows that the relative contribution from the HC[H] class increases with time, and this corresponds to an increase in the number of data points as seen in the DBE plots shown in Figure 7a. Figure 7a also shows the DBE plots shifting to higher carbon number over time, with the highest mass species eluting later in the GC run. While there was an increase in absolute intensity for all DBE between 20 – 30 min and 40 – 50 min, Figure 7b shows the change in relative contribution from each DBE to the overall HC[H] class intensity. DBE of 2.5 and below, and 6.5 and above, make a greater relative contribution at 40 – 50 min, while those between 2.5 and 5.5 inclusive make a greater contribution at 20 – 30 min, suggesting that they have a lower boiling point due to weaker intermolecular attractions, elute earlier as a result. A DBE of 6.5 in the HC[H] class corresponds to a neutral DBE of 7, the threshold for two fused benzene rings.

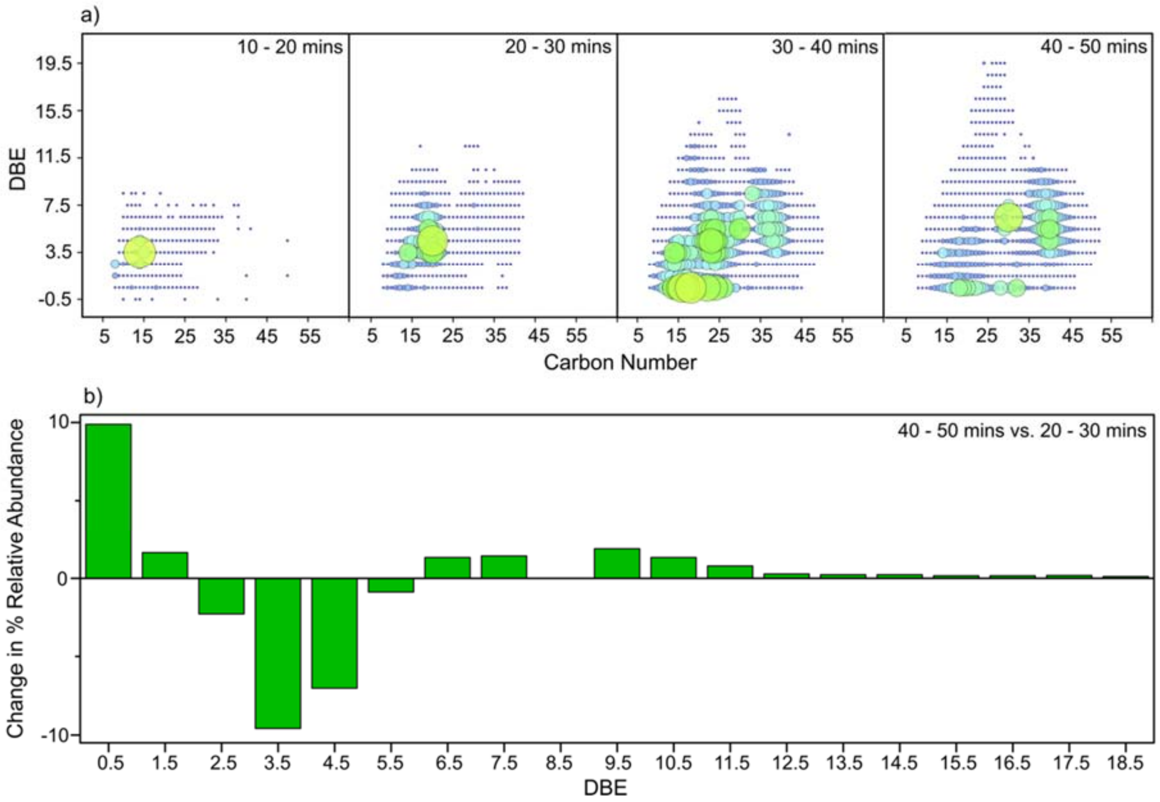

Figure 7. a) Plots of DBE against carbon number for the HC[H] class of sample depth 67.5 - 69.5 cm over 10 minute intervals of the GC run and b) Change in relative abundance of each DBE comparing the 40 - 50 min to the 20 - 30 min interval.

Further adding to the complexity of the data, EICs for a single data point within a DBE plot show that each molecular formula has a number of isomers associated with it. Figure 8 shows the EICs for the molecular formulae of three consecutive carbon numbers (24, 25, and 26), all with a DBE value of 6.5. Figure 8 shows the additional depth and complexity of data offered by the coupled GC-APCI FTICR MS technique, with each data point in the DBE against carbon number plots (Figure 7a) representative of multiple isomeric compounds.

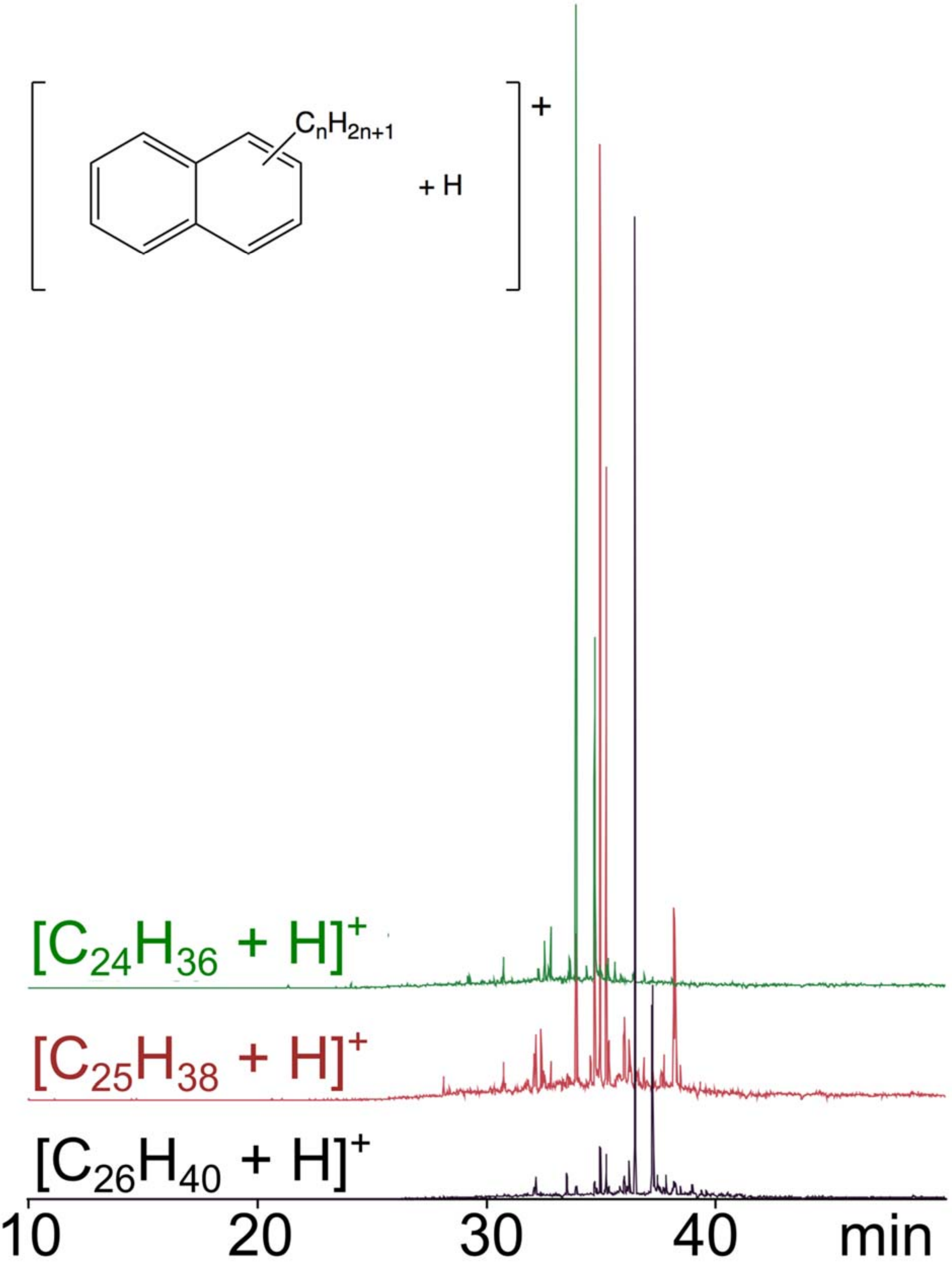

Figure 8. Extracted ion chromatograms for three molecular compositions, with sequential addition of CH_2. Each composition has DBE = 6.5, the threshold at which the potential core structure shown can form.

An enlargement of a 0.30 Da region is shown in Figure 9, comparing a spectrum acquired using direct infusion APPI FTICR MS on a 12 T solariX instrument and a spectrum acquired using GC-APCI-FTICR MS on a 7 T solariX

2XR instrument. Figure 9 shows not only the ultrahigh resolution capabilities of the 7 T 2XR instrument, comparable to that of the 12 T instrument, but also heteroatom class assignments only observed using the combined chromatographic separation and chemical ionization steps.

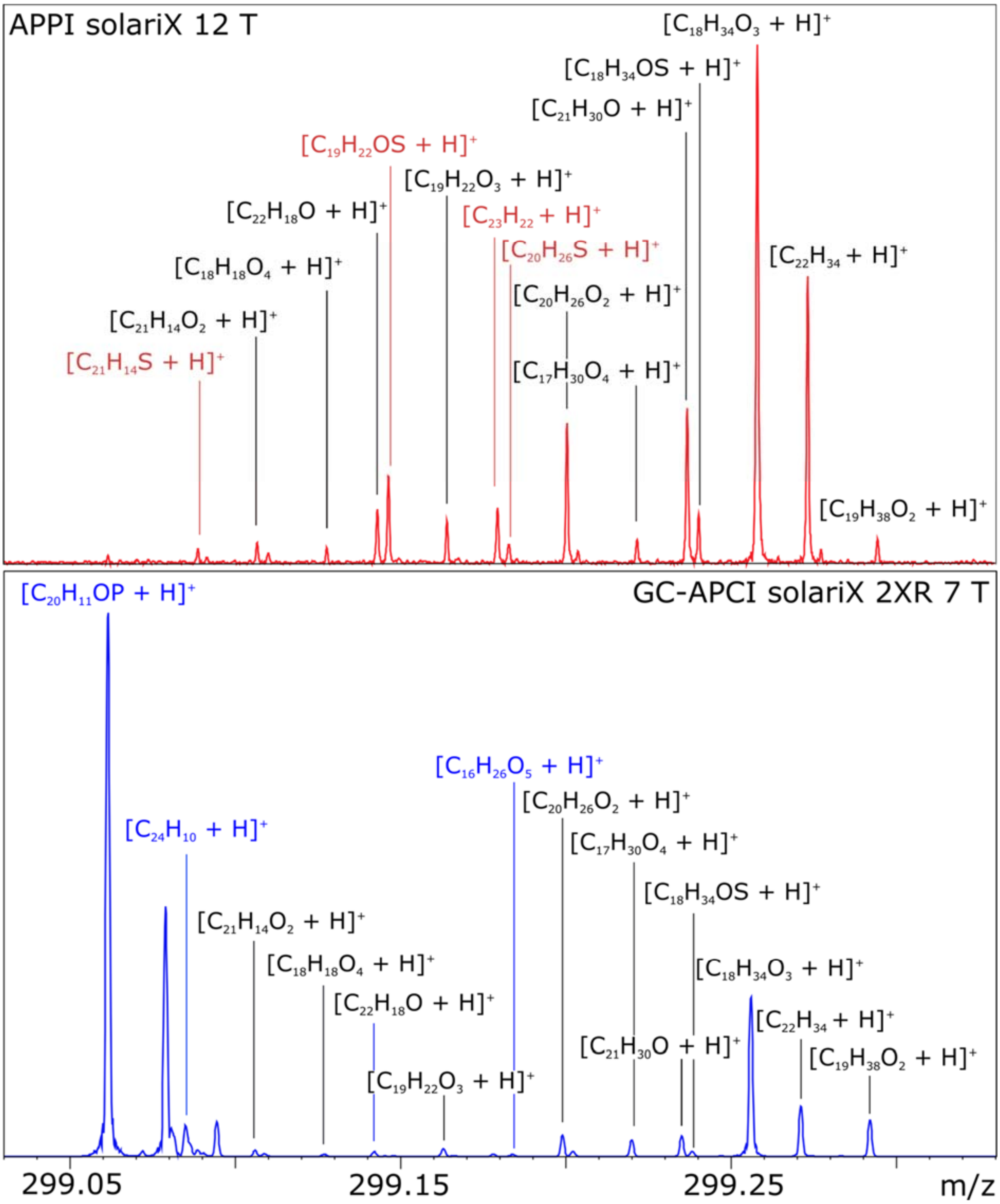

Figure 9. Enlarged 0.30 Da regions of the mass spectra obtained using a 12 T FTICR instrument equipped with an APPI ion source (top) and a 7 T FTICR instrument equipped with a GC-APCI source and 2ω detection (bottom) for the 67.5 - 69.5 cm sampling depth at 40 - 50 min retention time. A shift in the mass defect contribution as well as assignments unique to each spectrum are exemplified.

Figure 9 demonstrates the complementarity between the two techniques, with APPI ionizing hydrocarbon and S- containing species, and GC-APCI providing greater access to more highly oxygenated compounds. The differences in the preferential ionization of the two techniques is evidenced more generally by the higher relative intensity at lower mass defect for APCI, compared to greater relative intensity at higher mass defect in the APPI spectral window.

Conclusion

Several sampling depths with high hydrocarbon content were identified by bulk Rock-Eval pyrolysis, with key sampling depths that may be linked to major spills in the NY/NJ Estuary carried forward for further analysis. A sample that appeared to contain background levels of hydrocarbon compounds was also included. To complement the Rock-Eval data obtained for these soil depths, the key samples were profiled more extensively by direct infusion APPI FTICR MS, plus GC-APCI FTICR MS equipped with 2ω detection. Several trends in the compositional profile with were observed by direct infusion APPI-FTICR MS, including relatively high HC and O_xS_y[H] contributions at the sampling depths that corresponded to a spike in TOC and RC content by GC analyses. In general, the contribution from O_x and O_x[H] classes increased at these depths, which may be related to the aging of petroleum-related compounds. GC-APCI FTICR analysis identified additional groups more readily, including phosphorous containing compounds with low retention times, which may provide an indication of contamination by agrochemicals in the Estuary area. The sample that appeared to contain background levels of free and bound hydrocarbon by Rock-Eval pyrolysis was observed to contain many hydrocarbon and phosphorous compounds by APPI and GC-APCI FTICR MS, suggesting continuous pollution from petroleum and other industrial chemicals in the NY/NJ Estuary. Finally, the 7 T solariX 2XR instrument was shown to be capable of providing ultrahigh resolution data comparable to that obtained at the higher field of 12 T on sufficiently short timescales suitable for coupling with GC, demonstrating its viability as an emerging tool for the analysis of complex samples including petroleum and environmental samples.

SI

Full Compound Class Distribution Data (with time) – GC-APCI 2XR FTICR MS

Acknowledgements

Mary J. Thomas thanks EPSRC for a PhD studentship through the EPSRC Centre for Doctoral Training in Molecular Analytical Science, grant number EP/L015307/1.

The authors would also like to thank David Stranz, Sierra Analytics, for developments and access to Composer software.

Christopher H. Vane and Vick Moss-Hayes publish with permission of the Executive Director, British Geological Survey (BGS).

References

1. Packer, D. B., NOAA Technical Memorandum NMFS-NE-167. 1991. Assessment of characterisation of salt marshes in the Arthur Kill (New York-New Jersey) replanted after a server oil spill. 1991, pp. 232.
2. Gunster, D.G.; Gillis, C.A.; Bommevie, N.L.; Abel, T.B.; Wenning, R.J., Petroleum and hazardous chemical spills in Newark Bay, New Jersey, USA from 1982 to 1991. *Environmental Pollution* **1993**, *82*, 245-253.
3. Oros, D. R.; Ross, J. R. M., Polycyclic aromatic hydrocarbons in San Francisco Estuary sediments. *Marine Chemistry* **2004,** *86* (3-4), 169-184.

4. da Silva, D. A. M.; Bicego, M. C., Polycyclic aromatic hydrocarbons and petroleum biomarkers in Sao Sebastiao Channel, Brazil: Assessment of petroleum contamination. *Marine Environmental Research* **2010,** *69* (5), 277-286.

5. Vane, C.H.; Harrison, I.; Kim, A.W.; Moss-Hayes, V.; Vickers, B.P.; Horton., B.P. Status of Organic Pollutants in Surface Sediments of Barnegat Bay-Little Egg Harbor Estuary, New Jersey, USA. *Marine Pollution Bulletin* **2008**, 56 (10), 1802-1808

6. Vane, C.H.; Harrison, I.; Kim, A.W.; Moss-Hayes, V.; Vickers, B.P.; Hong, K. Organic and Metal Contamination in Surface Mangrove Sediments of South China. *Marine Pollution Bulletin* **2009**, 58, 134-144.

7. Vane, C.H.; Chenery, S.R.; Harrison, I.; Kim, A.W.; Moss-Hayes, V.; Jones, D.G. Chemical signatures of the Anthropocene in the Clyde Estuary, UK: Sediment hosted Pb, $^{207/206}$Pb, Polyaromatic Hydrocarbon (PAH) and Polychlorinated Biphenyl (PCB) pollution records. *Philosophical Transactions of the Royal Society (A)* **2011**, 369, 1085-1111

8. Langston, W. J.; O'Hara, S.; Pope, N. D.; Davey, M.; Shortridge, E.; Imamura, M.; Harino, H.; Kim, A.W.; Vane C.H. Bioaccumulation surveillance in Milford Haven Waterway. *Environmental Monitoring and Assessment* **2012**, 184 (1), 289-311**.**

9. Vane, C.H.; Moss-Hayes, V.; Kim, A.W.; Edgley, E.; Bearcock, J., Mercury (Hg), *n*-alkane and unresolved complex mixture (UCM) hydrocarbon pollution in surface sediment across rural-urban-estuarine continuum of the Clyde, UK. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh* **2018** (Accepted In-Press).

10. Alimi, H.; Ertel, T.; Schug, B., Fingerprinting of hydrocarbon fuel contaminants: Literature review. *Environmental Forensics* **2003,** *4* (1), 25-38.

11. White, H. K.; Xu, L.; Hartmann, P.; Quinn, J. G.; Reddy, C. M., Unresolved Complex Mixture (UCM) in Coastal Environments Is Derived from Fossil Sources. *Environmental Science & Technology* **2013,** *47* (2), 726-731.

12. Barrow, M. P., Petroleomics: study of the old and the new. *Biofuels* **2010,** *1* (5), 651-655.

13. Hsu, C.; Hendrickson, C.; Rodgers, R.; McKenna, A.; Marshall, A., Petroleomics: advanced molecular probe for petroleum heavy ends. *Journal of Mass Spectrometry* **2011,** *46* (4), 337-343.

14. Cho, Y.; Ahmed, A.; Islam, A.; Kim, S., DEVELOPMENTS IN FT-ICR MS INSTRUMENTATION, IONIZATION TECHNIQUES, AND DATA INTERPRETATION METHODS FOR PETROLEOMICS. *Mass Spectrometry Reviews* **2015,** *34* (2), 248-263.

15. Marshall, A.; Blakney, G.; Beu, S.; Hendrickson, C.; McKenna, A.; Purcell, J.; Rodgers, R.; Xian, F., Petroleomics: a test bed for ultra-high-resolution Fourier transform ion cyclotron resonance mass spectrometry. *European Journal of Mass Spectrometry* **2010,** *16* (3), 367-371.

16. Cho, E.; Witt, M.; Hur, M.; Jung, M.-J.; Kim, S., Application of FT-ICR MS Equipped with Quadrupole Detection for Analysis of Crude Oil. *Analytical Chemistry* **2017,** *89* (22), 12101-12107.

17. Schweikhard, L.; Lindinger, M.; Kluge, H. J., QUADRUPOLE-DETECTION FT-ICR MASS-SPECTROMETRY. *International Journal of Mass Spectrometry and Ion Processes* **1990,** *98* (1), 25-33.

18. Pan, Y.; Ridge, D. P.; Rockwood, A. L., HARMONIC SIGNAL ENHANCEMENT IN ION-CYCLOTRON RESONANCE MASS-SPECTROMETRY USING MULTIPLE ELECTRODE DETECTION. *International Journal of Mass Spectrometry and Ion Processes* **1988,** *84* (3), 293-304.

19. Schweikhard, L., THEORY OF QUADRUPOLE DETECTION FOURIER TRANSFORMION CYCLOTRON-RESONANCE. *International Journal of Mass Spectrometry and Ion Processes* **1991,** *107* (2), 281-292.

20. Tessarolo, N. S.; Silva, R. C.; Vanini, G.; Pinho, A.; Romao, W.; de Castro, E. V. R.; Azevedo, D. A., Assessing the chemical composition of bio-oils using FT-ICR mass spectrometry and comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry. *Microchemical Journal* **2014,** *117*, 68-76.

21. Wang, Z.; Fingas, M., Developments in the analysis of petroleum hydrocarbons in oils, petroleum products and oil-spill-related environmental samples by gas chromatography. *Journal of Chromatography a* **1997,** *774* (1-2), 51-78.

22. Beens, J.; Brinkman, U., The role of gas chromatography in compositional analyses in the petroleum industry. *Trac-Trends in Analytical Chemistry* **2000,** *19* (4), 260-275.

23. Lalli, P. M.; Jarvis, J. M.; Marshall, A. G.; Rodgers, R. P., Functional Isomers in Petroleum Emulsion Interfacial Material Revealed by Ion Mobility Mass Spectrometry and Collision-Induced Dissociation. *Energy & Fuels* **2017,** *31* (1), 311-318.

24. Blomberg, J.; Schoenmakers, P. J.; Brinkman, U. A. T., Gas chromatographic methods for oil analysis. *Journal of Chromatography A* **2002,** *972* (2), 137-173.

25. Schwemer, T.; Ruger, C. P.; Sklorz, M.; Zimmermann, R., Gas Chromatography Coupled to Atmospheric Pressure Chemical Ionization FT-ICR Mass Spectrometry for Improvement of Data Reliability. *Analytical Chemistry* **2015,** *87* (24), 11957-11961.

26. Slowakiewicz, M.; Tucker, M.E.; Vane, C.H.; Harding, R.; Collins, A.; Pancost, R.D. Shale-gas potential of the mid-Carboniferous Bowland-Hodder unit in the Cleveland Basin (Yorkshire), Central Britain. *Journal of Petroleum Geology* **2015**, 38, 1, 59-76.

27. Könitzer, S. F.; Stephenson, M.H.; Davies, J.; Vane, C.H.; Leng, M. J. Significance of sedimentary organic matter input for shale gas generation potential of Mississippian Mudstones, Widmerpool Gulf, UK. *Review of Palaeobotany and Palynology*, **2016**, 224 (2) 146-148.

28. Barrow, M.; Witt, M.; Headley, J.; Peru, K., Athabasca Oil Sands Process Water: Characterization by Atmospheric Pressure Photoionization and Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Analytical Chemistry* **2010,** *82* (9), 3727-3735.

29. Headley, J.; Barrow, M.; Peru, K.; Fahlman, B.; Frank, R.; Bickerton, G.; McMaster, M.; Parrott, J.; Hewitt, L., Preliminary fingerprinting of Athabasca oil sands polar organics in environmental samples using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Rapid Communications in Mass Spectrometry* **2011,** *25* (13), 1899-1909.

30. Chen, H.; Hou, A. X.; Corilo, Y. E.; Lin, Q. X.; Lu, J.; Mendelssohn, I. K.; Zhang, R.; Rodgers, R. P.; McKenna, A. M., 4 Years after the Deepwater Horizon Spill: Molecular Transformation of Macondo Well Oil in Louisiana Salt Marsh Sediments Revealed by FT-ICR Mass Spectrometry. *Environmental Science & Technology* **2016,** *50* (17), 9061-9069.

31. Zubair, A.; Pappoe, M.; James, L.; Hawboldt, K., Development, optimization, validation and application of faster gas chromatography - flame ionization detector method for the analysis of total petroleum hydrocarbons in contaminated soils. *Journal of Chromatography a* **2015,** *1425*, 240-248.

32. Rowland, S. M.; Robbins, W. K.; Marshall, A. G.; Rodgers, R. P., Characterization of Highly Oxygenated and Environmentally Weathered Crude Oils by Liquid Chromatography Fourier Transform Ion Cyclotron Mass Spectrometry (FT-ICR MS). *International Oil Spill Conference Proceedings* **2014,** *2014* (1), 300205.

33. Andrade, F. J.; Shelley, J. T.; Wetzel, W. C.; Webb, M. R.; Gamez, G.; Ray, S. J.; Hieftje, G. M., Atmospheric Pressure Chemical Ionization Source. 1. Ionization of Compounds in the Gas Phase. *Analytical Chemistry* **2008,** *80* (8), 2646-2653.

34. Benigni, P.; DeBord, J.; Thompson, C.; Gardinali, P.; Fernandez-Lima, F., Increasing Polyaromatic Hydrocarbon (PAH) Molecular Coverage during Fossil Oil Analysis by Combining Gas Chromatography and Atmospheric-Pressure Laser Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS). *Energy & Fuels* **2016,** *30* (1), 196-203.

35. Vane, C.H.; Harrison, I.; Kim, A.W. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediments from the Mersey Estuary, U.K. *Science of the Total Environment* **2007**, 374, 112-126.

36. Beriro, D. J.; Vane, C. H.; Cave, M. R.; Nathanail, C. P.; Effects of physical sample preparation on the concentrations of polycyclic aromatic hydrocarbons in gasworks contaminated soils. *Chemosphere* **2014**, 111, 396-404.

37. Environmental Protection Agency Method 3540C. (accessed February 2018).

38. Newell, A. J.; Vane, C. H.; Sorensen, J. P. R.; Moss-Hayes, V.; Gooddy, D. C. Long-term Holocene groundwater fluctuations in a chalk catchment: evidence from Rock-Eval pyrolysis of riparian peats. *Hydrological Processes* **2016**, 30 (24), 4556-4567

39. McLafferty, F. W.; Turecek, F., *Interpretation of Mass Spectra*. 4 ed.; University Science Books: Mill Valley, CA, 1993.

40. Marshall, A.; Rodgers, R., Petroleomics: Chemistry of the underworld. *Proceedings of the National Academy of Sciences of the United States of America* **2008,** *105* (47), 18090-18095.

41. Atlas, R. M., MICROBIAL-DEGRADATION OF PETROLEUM-HYDROCARBONS - AN ENVIRONMENTAL PERSPECTIVE. *Microbiological Reviews* **1981,** *45* (1), 180-209.

42. Wang, Z. D.; Fingas, M.; Blenkinsopp, S.; Sergy, G.; Landriault, M.; Sigouin, L.; Foght, J.; Semple, K.; Westlake, D. W. S., Comparison of oil composition changes due to biodegradation and physical weathering in different oils. *Journal of Chromatography A* **1998,** *809* (1-2), 89-107.

43. Douglas, G. S.; Bence, A. E.; Prince, R. C.; McMillen, S. J.; Butler, E. L., Environmental stability of selected petroleum hydrocarbon source and weathering ratios. *Environmental Science & Technology* **1996,** *30* (7), 2332-2339.

44. New York, New York - Fresh kills landfill closes. *Biocycle* **2001,** *42* (4), 22-23.