Project Title	**Investigation of the effects of transport infrastructure upon the environment using ultrahigh resolution mass spectrometry**
University (where student will register)	University of Warwick
Which institution will the student be based at?	As above
Theme (Max. 2 selections)	Climate & Environmental Sustainability ☒ Organisms & Ecosystems ☐ Dynamic Earth ☐
Key words	**Fourier transform ion cyclotron resonance mass spectrometry, geochemistry, complex mixtures**
Supervisory team (including institution & email address	**PI: Dr. Mark P. Barrow (University of Warwick, E-Mail: M.P.Barrow@warwick.ac.uk)** **Co-I: Dr. Christopher H. Vane (British Geological Survey, E-Mail: chv@bgs.ac.uk)**

Project Highlights:

- **State-of-the-art mass spectrometry instrumentation (amongst world-leading)**
- **Environmental research with an international outlook**
- **Supervisory team consists of leaders in organic geochemistry and complex mixture analysis**
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Overview:

Bitumen roadways play a critical role in the economic and social development that is the corner stone of ever-increasing urbanisation across the globe. The UK has a network of about 400,000 km paved roads containing bitumen sourced from the distillation of crude oil and or coals which can contain environmentally harmful organic compounds. Whilst common organic pollutants such as polyaromatic hydrocarbons (PAH) are measured in soil and sediment surveys there is a lack of knowledge concerning roadways and their impact on surrounding urban soils and sediments. This partly stems from the fact that the precise chemical composition of its principal organic constituents, namely, saturated and aromatic hydrocarbons, asphaltenes and resins varies depending on the source crude oil and refining/distillation process used. These characteristics and variations also hinder our ability to truly comprehend the potential for toxic effects resulting from the presence of these compound classes.

There is a strong need for improved methodologies for environmental monitoring, particularly with respect to understanding the chemistry of highly complex samples. Ultrahigh resolution mass spectrometry, such as Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS), is a state-of-the-art analytical method which has been playing a leading role in the modern characterization of complex mixtures. The technique produces complex data sets which subsequently serve as molecular “profiles” or “fingerprints” of the organic components. The detailed molecular characterization of samples, typically including tens of thousands of organic compositions, can be

processed, visualized, and compared using a variety of methods. Collaboration with the Department of Statistics has also resulted in significantly improved processing of complex data sets and the production of in-house software, used in conjunction with commercial data analysis software. A recent example of collaboration with the British Geological Survey has included a study of soil cores from Staten Island (USA), where analysis of soil from varying depths provides a chemical history of oil contamination in the region. This PhD seeks to use state-of-the-art methods to model processes in the environment and to characterize real world samples to gain greater insights into the impact of UK roadways upon the environment.

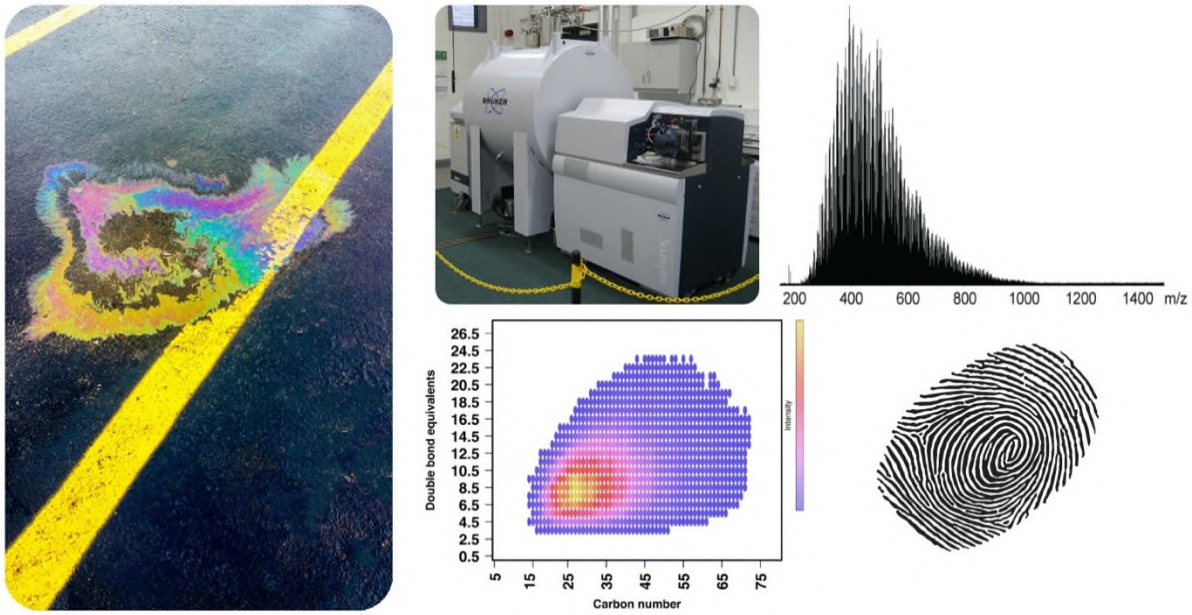

Figure 1: *From real world sample to analysis by a 12 T Bruker solariX FTICR mass spectrometer. The data can be analyzed and visualized, producing a detailed molecular fingerprint for individual samples.*

Methodology:

Dr. Vane and his team at the British Geological Survey (BGS) will provide samples of national and international sites of interest and expertise in hydrocarbon analyses by gas chromatography-mass spectrometry (GC/MS), while Dr. Barrow and his research group will provide expertise for the 12 T FTICR mass spectrometer. Ultrahigh resolution mass spectrometry will offer new information for a range of environmental samples, where lower resolution techniques provide less detailed profiles and key details can be lost. Sample collection in the environment, sample extraction/preparation methods in the laboratory, ionization methods, and fragmentation methods will be explored to develop a fuller picture of the composition of complex samples. State-of-the-art data analysis methods, originally arising from research into petroleum analysis, will be used to analyze the visualize the data, where samples can then be compared. Data processing methods will also be explored to optimize the sample comparisons.

Training and skills:

Students will be awarded CENTA2 Training Credits (CTCs) for participation in CENTA2-provided and 'free choice' external training. One CTC equates to 1⁄2 day session and students must accrue 100 CTCs across the three years of their PhD.

The student will gain training and expertise in the field of organic geochemistry, including sample collection and preparation, and complementary analytical methods (Iatroscan, Rock-Eval(6) pyrolysis, GC/MS). The student will spend at least three months working in-house at the BGS. At the University of Warwick, the student will gain expertise from one of the world's leading FTICR laboratories, learning FTICR mass spectrometry and including use of different ionization, fragmentation, and data analysis techniques.

Partners and collaboration (including CASE):

Dr. Barrow has approximately 20 years of experience of working with FTICR mass spectrometry, petroleum-related samples, environmental samples, and data analysis and visualization of complex mixtures, collaborating with industry and with environmental organizations. Dr. Vane has 22 years of experience in the field of organic geochemistry, and has been working with the BGS since 2001. This project is a Collaborative Studentship with the British Geological Survey (BGS) and the BGS supervisor (C. Vane) has applied to the BGS University Funding Initiative (BUFI) for an additional £7,700 to cover the analytical and field collection costs and augment the student's RSTG.

COVID-19 Resilience of the Project:

The Ion Cyclotron Resonance Laboratory has assessed the circumstances pertaining to the coronavirus pandemic and has established new working practices that enable safe continuation of research. The focus of the mitigation efforts has been the acquisition of new FTICR data and the laboratory reopened during the summer of 2020. Arrangements have also been put in place which permit remote data analysis and remote meetings, which grant researchers increased flexibility and offer a resilient approach should there be a resurgence of the coronavirus. BGS, OGF reopened in May 2020 with modified field laboratory protocols and individual office space.

Possible timeline:

Year 1: Introduction to FTICR mass spectrometry, training on the 12 T solariX, introduction to data analysis methods, analysis of initial samples

Year 2: Training in how to collect samples from key core intervals, introduction to standard petroleum environmental analyses including total Petroleum hydrocarbons (TPH) by iatroscan and parent and alkylated polyaromatic hydrocarbons by GC/MS/MS as well as data interrogation tools (BGS). Characterization of chemical composition of different bitumen/asphalt surfaces and sealants used in urban UK using FTICR MS. Quantification and evaluation of the bitumen sourced road run-off in a rural, peri-urban and urban setting

Year 3: Evaluation of compounds to identify sources (provenance) using FTICR MS. Generation of samples in the laboratory to model transformation in the environment. Integration of all FTICR MS and traditional geochemistry data sets to investigate chemical fingerprinting of real world samples

with the aim understanding contamination of the environment; evaluation of the chemistry to assess possible environmental and human health effects.

Further reading:

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Palacio Lozano, D.C., Gavard, R., Arenas-Diaz, J.P., Thomas, M.J., Stranz, D.D., Mejía-Ospino, E., Guzman, A., Spencer, S.E.F., Rossell, D. & Barrow, M.P. (2019) "Pushing the analytical limits: new insights into complex mixtures using mass spectra segments of constant ultrahigh resolving power." *Chem Sci*, 10(29), pp. 6966-6978.

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Further details:

For further information, please contact Dr. Vane or Dr. Barrow directly, and see the research group web sites:

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