Project Title	**Investigating the environmental impact of the Athabasca oil sands industry using ultrahigh resolution mass spectrometry**
University (where student will register)	University of Warwick
Theme (Max. 2 selections)	Climate & Environmental Sustainability ☒ Organisms & Ecosystems ☐ Dynamic Earth ☐
Key words	**Fourier transform ion cyclotron resonance mass spectrometry, FTICR MS, petroleomics, environmental, complex mixtures, industry, oil sands**
Supervisory team (including institution & email address	**PI:** **Dr. Mark P. Barrow** **(University of Warwick, E-Mail: M.P.Barrow@warwick.ac.uk)** **Co-I:** **Prof. Gary Bending** **(University of Warwick, E-Mail: gary.bending@warwick.ac.uk)** **Dr. John V. Headley** **(Environment and Climate Change Canada, E-Mail: john.headley@canada.ca)** **Dr. Jason Ahad** **(GSC-Quebec, E-Mail: jason.ahad@NRCan-RNCan.gc.ca)**

Project Highlights:

- **State-of-the-art mass spectrometry instrumentation (amongst world-leading)**
- **International environmental research**
- **Supervisory team consists of world leaders in oil sands, soil microbial profiling, and complex mixture analysis**

Overview (including 1 high quality image or figure): Maximum 350 words

The oil sands industry in Alberta, Canada, represents an alternative source of petroleum which has positioned Canada as the leading supplier of oil to the USA. The oil sands material consist of clay, sand, water, and bitumen, where the bitumen can be extracted using an alkaline hot water extractions process. Approximately three barrels of water are needed to produce one barrel of oil but this water, oil sands process affected water (OSPW), cannot be discharged back into the environment, due to federal regulations. As a result, the OSPW is stored in vast tailings ponds, currently estimated to hold approximately 1 trillion litres of water. The vast amounts of tailings pond waters contain substances that are known to be toxic to aquatic environments. For example, recent studies have implicated a wide range of classical naphthenic acids as principal toxicants, along with heavy metals and salts. The anthropogenic impact of future release of OSPW upon the aquatic environment is thus of increasing concern. There is a strong need for improved methodologies for characterization of the oil sands naphthenic acids for environmental monitoring, particularly with respect to understanding the chemistry of highly complex environmental samples. The comprehensive characterization of the organic fraction of OSPW with regards to fate and transport in aquatic environments is not yet established. Ultrahigh resolution mass spectrometry, particularly Fourier transform ion cyclotron resonance (FTICR) mass spectrometry (MS), has played a key role in the molecular characterization of environmental samples, leading to complex data sets which subsequently serve as "profiles" or "fingerprints" of the organic components in OSPW. The proposed work will, for the first time, utilize advances in proprietary software tools, developed at the University of Warwick, to improve and expand the molecular characterization of principal toxic components in OSPW, including providing greater insight into isomeric structures.

Figure 1: *Athabasca oil sands processing facility, north of Fort McMurray (Alberta, Canada) and adjacent to Athabasca River.*

Methodology: **Maximum 150 words**

This study will fingerprint oil sands processed waters collected from the Athabasca oil sands region, along with groundwater overlying undeveloped shale gas and tight oil reservoirs in Canada. A better understanding of the influence of environmental processes upon the molecular profiles is required, as it can be used to build a model of the environmental fate of oil sands components. In order to address this, the transport of oil sands components through soil and their subsequent microbial degradation will be experimentally investigated in the laboratory. The resulting samples will be characterized using ultrahigh resolution mass spectrometry; one of the smallest mass differences commonly observed in the mass spectra of naphthenic acid mixtures is 3.4 mDa, resulting from the complex mixture rich in O_x and SO_x isobars. The project will also refine the interpretation and comparison of MS data to better characterize naphthenic acids in aquatic environments.

Training and skills: **Maximum 1000 words**

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 environmental analysis, including sample collection and preparation. The student will have the option to work in-house in Saskatoon, Canada, with the research team of Dr Headley. This international exposure will provide hands-on training in oil sands environmental chemistry. 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):

Name of L1/L2 Partner (where applicable)	
Name of CASE partner (where applicable – project proposal **must** be accompanied by a letter of support from the CASE partner)	

Further information on partners and collaboration (including CASE): *Maximum 100 words*

Dr. Barrow has approximately 20 years of experience of working with FTICR mass spectrometry, petroleum-related and environmental samples, and data analysis of complex mixtures, collaborating with industry and with environmental organizations. Prof. Bending provides expertise on microbial profiling, metagenomics, and soil microcosm type systems. Dr. Headley has approximately 40 years of research experience (more than 26 years of working at Environment and Climate Change Canada) and is amongst the world's leading experts on the oil sands industry. Dr. Ahad has conducted his research in Canada and the UK, and has been working with GSC-Quebec for more than 13 years.

Respiratory and Contact Infection Resilience of the Project: *Maximum 100 words:*

Please give concise information about how any respiratory and contact infection pandemic might potentially affect project delivery and how far mitigation efforts can be made available. Give a clear overview of those mitigation efforts, if the project or parts of it might be affected. If a shift of topic would be possible, please indicate in which direction any adjustment could be made. Please note: Project proposals without respiratory and contact infection resilience information will not be advertised.

The Ion Cyclotron Resonance Laboratory has assessed the circumstances pertaining to the coronavirus pandemic, carried out risk assessments from 2020 onwards, and has established new working practices that enable flexibility and safe continuation of research. With multiple options for sources of samples, research projects are highly adaptable should there be an unforeseen change in direction. Arrangements have also been put in place which permit remote data analysis and remote meetings at/between Warwick and collaborators in Canada, which grant researchers increased flexibility and offer a resilient approach should there be a resurgence of the coronavirus.

Possible timeline:

Year 1: Introduction to FTICR mass spectrometry, training on the 12 T solariX and 15 T solariX XR, introduction to data analysis methods, analysis of initial samples

Year 2: Intent to coordinate field sampling during two week period with collaborators (Dr. Jason Ahad) for shale gas and tight oil reservoirs in Canada.

Year 3: Focus of the work will be Athabasca oil sands region, along with groundwater overlying undeveloped shale gas and tight oil reservoirs.

Further reading:

Barrow, M.P., Peru, K.M. & Headley, J.V. (2014) "An Added Dimension: GC Atmospheric Pressure Chemical Ionization FTICR MS and the Athabasca Oil Sands." *Anal. Chem.*, 86(16), pp. 8281-8288.

Barrow, M.P., Witt, M., Headley, J.V. & Peru, K.M. (2010) "Athabasca Oil Sands Process Water: Characterization by Atmospheric Pressure Photoionization and Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry" *Anal. Chem.*, 82(9), pp. 3727-3735.

Barrow, M.P., Peru, K.M., McMartin, D.W. & Headley, J.V. (2016) "Effects of Extraction pH on the Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Profiles of Athabasca Oil Sands Process Water" *Energy & Fuels*, 30(5), pp. 3615-3621.

Headley, J.V., Barrow, M.P., Peru, K.M., Fahlman, B., Frank, R.A., Bickerton, G., McMaster, M.E., Parrott, J. & Hewitt, L.M. (2011) "Preliminary fingerprinting of Athabasca oil sands polar organics in environmental samples using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry." *Rapid Commun. Mass Spectrom.*, 25(13), pp. 1899-1909.

Headley, J.V., Peru, K.M. & Barrow, M.P. (2016) "Advances in mass spectrometric characterization of naphthenic acids fraction compounds in oil sands environmental samples and crude oil-a review." *Mass Spectrom. Rev.*, 35(2), pp. 311-328.

Lozano, D.C.P., Thomas, M.J., Jones, H.E. & Barrow, M.P. (2020) “Petroleomics: Tools, Challenges, and Developments” *Annual Review of Analytical Chemistry*, 13, pp. 405-430.

Peru, K.M., Thomas, M.J., Palacio Lozano, D.C., McMartin, D.W., Headley, J.V. & Barrow, M.P. (2019) “Characterization of oil sands naphthenic acids by negative-ion electrospray ionization mass spectrometry: Influence of acidic versus basic transfer solvent” *Chemosphere*, 222, pp. 1017-1024.

Further details:

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