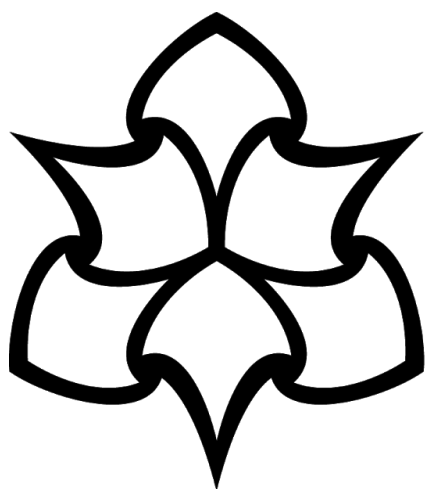


# British Organic Geochemical Society

## 2019 Meeting Programme and Abstracts



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# British Organic Geochemical Society

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## WEDNESDAY 10th JULY

**09:00**

Arrival, registration

Coffee and pastries

**09:30**

Opening remarks

Welcome, health and safety, logistics

### Session 1: The Carbon Cycle

Session chair: Gordon Inglis

**09:40**

1. Sara Trojahn

The role of seasonal trends and rain events in carbon export of Scottish peat-dominated headwater streams

**10:00**

2. Saule Akmetkaliyeva

Carbon release during 21st century glacier recession: A positive feedback in the global carbon cycle

**10:20**

3. Sevda Norouzi  
Alibabalou

Constraining the Gas Transfer between Atmosphere and Water Streams of Tropical Rainforests of Guyana

**10:40**

4. Coleen Murty

Molecular characterization of Sphagnum-derived phenolics and their role in peatland carbon cycling

**11:00**

Break

Coffee

### Session 2: Palaeo (climate and ontology)

Session chair: Yvette Eley

**11:30**

5. Emily Dearing  
Crampton-Flood

Towards reliable reconstructions of Pliocene terrestrial temperatures using branched tetraether membrane lipids

**11:50**

6. Caitlyn Witkowski

Decline of PCO<sub>2</sub> from the Miocene based on the δ<sup>13</sup>C of algal biomarkers

**12:10**

7. Bart van Dongen Mapping of pigment remnants in fossils

**12:30**

Break Hot buffet lunch

### Session 3: Pollution Monitoring and Remediation

Session chair: Sophie Nixon

**13:30**

8. Katrina Cullen The impact of environmental parameters on the adsorption of azo dyes on Nyex™

**13:50**

9. Daniel Niepsch Lichen biomonitoring to assess spatial variability of airborne polycyclic aromatic hydrocarbons (PAHs) in Manchester, UK

**14:10**

10. Rakiya Muhammad Assessing the impacts of oil contamination on soil microbial community/diversity in the Niger Delta (Nigeria)

**14:30**

Poster talks One minute slide by each poster presenter

**14:50**

Break Coffee and pastries

### Session 4: Posters and Keynote

**15:00**

Poster Session Beer, wine and soft drinks

**16:30**

11. Jaime Toney Biomarker development and deciphering environmental signals

**17:30**

Break Walk / transfer to conference dinner

**18:30**

Conference Dinner Croma Restaurant, Clarence St, Manchester, M2 4DE

**21:30**

Drinks and Discussion Brewdog, 35 Peter St, Manchester, M2 5BG



## LIST OF POSTERS

19. Abigail Savage GDGTs and BHPs in glacial lakes from Northeastern Greenland
20. Alexander D. Mutshow Effect of Weathering on Markers used in Oil Fingerprinting
21. Alice Hardman The Development of 3-Hydroxy Fatty Acid-Based Palaeoclimate Proxies
22. Bridget Warren Development and application of novel ecological and environmental proxies from leaf wax lipids
23. David Jones Assessing organic and heavy metal pollution in post-industrial Manchester
24. Emma Burns Fate of Terrigenous Nitrogen in Arctic Shelf Sediments - An update
25. James Bendle Biomarkers in Stalagmites: Reconstructing Temperature, Hydrology, Vegetation and Bacterial Responses to Climate Change.
26. Jonathan Hall Mid-Pliocene North Atlantic warming: an insight from marine and terrestrial records
27. Martina Conti A New Approach for Studying Past Sea-level Changes Using Molecular Fossils
28. Matthew Carney brGDGT Lipid Biomarkers as a Post-Glacial Environmental Proxy
29. Mingda Wang What does lacustrine sedimentary n-alkane average chain length from the Tibetan Plateau tell us?
30. Natta Wiriyakun Alternative Approach to the Measurement of Cholesterol and Cholestanols as Signatures of Human Activity in Archaeological Contexts
31. Sharon Fraser Resinous Coating of Takabuti - the Belfast Mummy
32. Yvette Eley OPTiMAL: A new machine learning approach for GDGT-based palaeothermometry

# The role of seasonal trends and rain events in carbon export of Scottish peat-dominated headwater streams

Sara Trojahn<sup>1\*</sup>, Ryan Pereira<sup>1</sup>, Juliane Bischoff<sup>1</sup>, Thomas Wagner<sup>1</sup>, Bryan M. Spears<sup>2</sup>, Amy Pickard<sup>2</sup>

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Weather, Hydrology and organic matter flux are closely inter-linked and seasonal differences can be observed. Superimposed on the seasonal cycle, rain events have the potential to mobilise large amounts of organic carbon and nutrients from vegetation and soils of the surrounding landscape which can be magnified after extended dry periods. This results in a large variability in the composition and potential reactivity of dissolved organic matter (DOM) along headwater river systems. Peat-dominated catchments are particularly vulnerable to weather extremes and have the potential to release large quantities of organic carbon, providing a positive feedback to atmospheric greenhouse gas emission (Billett et al. 2004, Clark et al. 2007).

We investigated the riverine carbon exports from a two headwater peatland environments in the UK, and examined the potential uncertainty of quantification due to the role of optically “invisible” dissolved organic matter (iDOM). Importantly, our work captured compositional changes of riverine DOM in during an exceptionally dry period and compared these with rain events during a generally wetter cooler period in 2018, perhaps an analogue of future climate and weather scenarios. A novel size exclusion chromatography technique allowed elucidation of five different DOM pools including Humics to Biopolymers, Building Blocks, lower molecular weight (LMW) Acids, and LMW Neutrals, without isolating or modifying the original sample.

Our results show that high temporally resolved sampling of our headwater rivers is required to capture notable changes in DOM composition from humic dominated to LMW organic substances. We also found that during rain intensive periods predominantly humic based substances are mobilised (~80-90% of the total DOM pool) in summer and winter. Conversely, during longer dry periods the amount of LMW DOM increased by up to 60% in one of the headwaters, becoming the more dominant pool of organic matter in the river. Importantly, this LMW DOM consists of ‘neutral’ compounds that are not amenable to UV-Vis absorbance of fluorescence measurements and are therefore “invisible” to typically utilised in-situ and remote sensing measurement approaches.

This implies that riverine carbon fluxes are under quantified from peat-dominated environments, especially as these LMW compounds are not observed downstream (~2km) indicating a highly labile DOM component is remineralised within the water column.

References:

Billett et al. (2004) DOI: [10.1029/2003gb002058](https://doi.org/10.1029/2003gb002058). Clark et al. (2007) DOI: [10.1016/j.jhydrol.2007.09.030](https://doi.org/10.1016/j.jhydrol.2007.09.030).

# Carbon release during 21st century glacier recession: A positive feedback in the global carbon cycle

Saule Akhmetkaliyeva<sup>1\*</sup>, Robert Sparkes<sup>1</sup>, Leon Clarke<sup>1</sup>, Andrew Dean<sup>1</sup>, Simon Cook<sup>2</sup>

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Glaciers cover 11% of Earth's surface and contain significant reserves of glacial organic carbon (GOC). Much of the GOC is stored within glacial ice, subglacial and proglacial sediment and soils in northern latitudes, and is discharged as glaciers recede. When GOC in the form of dissolved and particulate organic carbon, and nutrients, are released as glaciers melt, potent greenhouse gases are released into the atmosphere creating positive feedback on global warming, as well as seeding biological production downstream. However, despite the importance of GOC its release from receding glaciers in the Arctic and Subarctic regions has not been previously studied in detail. Therefore, this study aims to elucidate the role of GOC as a carbon source in the dynamic Arctic and Subarctic regions by comparing carbon transportation in two contrasting glacial systems (Oræfajökull ice cap in Iceland and Tarfala in Sweden). This is being achieved by understanding the main source of GOC and downstream microbial metabolism of released GOC, which will allow us to quantify GOC and nutrient fluxes, and to understand the organic carbon transformations along the downstream transect from the glacial front. Water, soil and sediment samples have been collected as a result of two successful field campaigns to Iceland and Sweden in summer 2018. Dissolved organic carbon (DOC) analysis of meltwater showed that an average concentration in Icelandic glacial melt ranges from 1.305 mg/L to 13.205 mg/L, while in Sweden the numbers vary from 0.593 mg/L to 19.402 mg/L. Generally, proglacial lakes have higher DOC concentrations compared to meltwater streams and river samples, which is most likely caused by microbial OC production driven by sedimentation and longer residence time in the same basin. In addition, soil and sediment samples were analysed for total and organic carbon and nitrogen concentrations. Soil samples from moraines in front of Svínafellsjökull showed highest organic carbon concentration (up to 5.5%) in Iceland, and the samples from the bank of the Tarfala lake yielded highest results (0.7%) in Sweden, while sediment samples from both study areas barely had any carbon signal. Based on the results obtained from carbon and nitrogen analysis, 28 soil and sediment samples with highest total organic carbon concentrations to ensure effectiveness of further analysis were selected for organic biomarker identification. Preliminary results from biomarker analysis show clear signs of soil markers in soil samples. These data combined with other analyses such as the elemental, ionic and isotopic concentrations, microbiological DNA extractions of collected glacial meltwater and proglacial lake water, soil and sediment samples will facilitate assessment of how released carbon is mobilized, eroded and degraded in deglaciating systems in the Arctic (Sweden) and Subarctic (Iceland) regions.



# Constraining the Gas Transfer between Atmosphere and Water Streams of Tropical Rainforests of Guyana

Sevda Norouzi Alibabalou<sup>1\*</sup>, Alan MacDonald<sup>2</sup>, Sara Trojahn<sup>1</sup>, Juliane Bischoff<sup>1</sup>, James Spray<sup>1</sup>, Thomas Wagner<sup>1</sup>, Andrew Tye<sup>3</sup>, Ryan Pereira<sup>1</sup>

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Greenhouse gases can alter Earth's climate by absorbing energy in the lower atmosphere and re-emitting it which can affect climate for decades to millennia after being emitted (Montzka et al., 2011). Understanding and quantifying water–atmosphere exchanges of the greenhouse gases (GHG), such as CO<sub>2</sub>, are of great importance for understanding the global biogeochemical cycling of carbon and its impact on future climate.

Constraining the gas transfer rates of GHGs between water and the atmosphere, and determining the primary and secondary processes that control gas transfer velocity ( $k$ ) are critical for improved understanding of the carbon cycle in all aquatic systems along the land-ocean continuum. The majority of gas transfer, water–atmosphere studies are focussed on the marine environment (Bakker et al., 2014; Pereira et al., 2018) where wind and wave turbulence are primary factors but bubbles and surface-layer organic substances have been recently identified as important secondary factors that significantly reduce the overall uncertainties of gas transfer rate estimates. Much less is known in river systems and tropical rivers in particular (Raymond et al., 2013). The topographic slope is a key factor that influences  $k$  in streams (Raymond and Cole, 2001; Wallin et al., 2011); however, the gas exchanges in tropical lowland rivers such as the Amazon, Orinoco and Essequibo (the three largest rivers in South America) are more likely influenced by surface turbulence (e.g. wind) and the role of organic substances in the surface microlayer that can reduce the gas exchange at the water–atmosphere interface.

Here we present the first preliminary results of water–atmosphere CO<sub>2</sub> fluxes of Amazonian headwaters in the Essequibo River during the dry-wet season transition in 2019. Importantly we will show the changes in the flux of CO<sub>2</sub> in relation to compositional changes of dissolved organic matter (DOM) in the river surface micro-layer. A key focus will be on rain events and their role in riverine CO<sub>2</sub> emissions.

# Molecular characterization of *Sphagnum*-derived phenolics and their role in peatland carbon cycling

C. Murty<sup>1</sup>, C. H. Vane<sup>2</sup>, A. Charlton<sup>1</sup>, N. Gray<sup>1</sup>, G. D. Abbott<sup>1</sup>

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Northern peatlands are powerful agents of carbon sequestration and storage, having the ability to accumulate vast amounts of carbon (C) over millennial timescales with low risks of leakage to the atmosphere. *Sphagnum* moss is the dominant peat-forming species across northern, boreal regions and is responsible for the high carbon storage densities observed in ombrotrophic peats. Phenolic compounds play an essential role in carbon accumulation and stabilization in peatland ecosystems by acting as anti-microbial agents, effectively inhibiting the decay of organic matter in surficial oxic peat layers. Sphagnum acid is one of the major phenolics exclusively biosynthesised by *Sphagnum* moss, it contributes to suppression of litter decomposition and vascular plant growth. Despite this, the molecular nature, mobility and persistence of the phenolic compounds released from *Sphagnum* moss in drought conditions remains unclear.

This research aims to disentangle the fate of phenolics leached from peat and moss, and characterize their associated transformation/degradation products. Previous research in our laboratory has demonstrated that 'bound' *Sphagnum* phenolics are degraded under aerobic conditions and lost to the environment (Abbott *et al.*, 2013; Schellekens *et al.*, 2015a, b; Swain and Abbott, 2013). Yet, the stability and ultimate fate of 'free' phenolics is yet to be investigated. Here, we use a combination of geomolecular techniques to track individually targeted phenolic acids derived from one of the largest, most valuable *Sphagnum*-dominated wetlands in the UK, namely Butterburn Flow. By developing an UPLC-ESI-MS/MS method for the identification of water-soluble phenolics, we are tracking associated derivatives/degradation products in natural waters and aqueous peat/moss extracts. Phenolic acids are identified based on their mass spectra and retention times compared to that of authentic standards.

Monitoring the degradation of dissolved phenolics under both aerobic and anaerobic conditions can reveal how stable/unstable they may be at different depths of the peatland and pinpoint their main degradation pathways. Observing variations in the nature and abundance of phenolics present down peat profiles across a transitional mire will help us elucidate the different mechanisms of how carbon is lost and sequestered in ombrotrophic and minerotrophic peatland ecosystems.

## References

Abbott *et al.* (2013) *Geochimica et Cosmochimica Acta*, 106, pp. 177-191.

Schellekens *et al.* (2015a) *Geochimica et Cosmochimica Acta*, 150, pp. 74-89.

Schellekens *et al.* (2015b) *Quaternary Science Reviews*, 123, pp. 254-264.

Swain, E.Y., Abbott, G.D., (2013) *Journal of Analytical and Applied Pyrolysis*, 103, pp. 2-7.

# Towards reliable reconstructions of Pliocene terrestrial temperatures using branched tetraether membrane lipids

Emily Dearing Crampton-Flood<sup>1\*</sup>, Damian Smits<sup>1</sup>, Guido van der Molen<sup>1</sup>, Lars J. Noorbergen<sup>2</sup>, Lucas Lourens<sup>1</sup>, Dirk K. Munsterman<sup>3</sup>, C. van der Weijst<sup>1</sup>, Timme Donders<sup>1</sup>, F. Peterse<sup>1</sup>, J. S. Sinninghe Damsté<sup>1,4</sup>

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The Mid-Piacenzian Warm Period (mPWP, ca. 3.3-3.0 Ma) is a frequently targeted interval for model simulations because it is considered to be an analogue for the climate of the mid-21<sup>st</sup> century. CO<sub>2</sub> levels, continental configurations, land elevations, and ocean bathymetry during the mPWP were comparable to present. However, global temperatures were warmer by 2-4 °C, indicating that current climate may not have reached equilibrium. While sea surface temperature (SST) reconstructions for the mPWP are abundant, temperatures in the terrestrial realm remain poorly constrained due to the scarcity of stratigraphically complete terrestrial sedimentary archives and a lack of quantitative proxies for mean air temperature (MAT).

Branched glycerol dialkyl glycerol tetraethers (brGDGTs) have emerged as a promising proxy for terrestrial MAT reconstruction, as the relative distribution of these bacterial membrane lipids in soils correlates with MAT (Weijers et al., 2007). Upon mobilization and subsequent transport from land to sea by rivers, these soil-derived brGDGTs are buried in the coastal marine sedimentary archive, where they should represent an integrated climate signal of the catchment area. Despite their presumed soil-origin, recent studies indicate that brGDGTs can also be produced in the coastal marine environment, which may alter the initial soil signature. Thus, brGDGTs should only be used as paleothermometer at sites where a substantial terrestrial input is expected.

Here, we aim to produce continental air temperature records for the Pliocene using brGDGTs in continental margin and continental shelf sediments. We target three sites that are all located relatively close to the mouth of a major river that was active during the Pliocene: ocean drilling program (ODP) Site 925 on the Ceará Rise (Amazon outflow), ODP Site 625 in the Gulf of Mexico (GoM, Mississippi outflow), and the Hank borehole in the Netherlands (Rhine-Meuse outflow).

Although brGDGTs were present in the GoM sediments, extremely low (0.002-1) branched to isoprenoid tetraether (BIT) index values, a ratio of soil-derived to marine-derived tetraethers, indicates that this site did not receive a substantial amount of terrestrial organic matter in the Pliocene. This is confirmed by the low amounts of pollen and plant leaf waxes in this core. Moreover, the high (0.5-0.7) weighted average of the number rings in the tetramethylated brGDGTs ( $\#rings_{tetra}$ ; Sinninghe Damsté, 2016) indicates that most of the brGDGTs have a marine origin, which disqualifies this site for continental paleotemperature reconstruction. In contrast, both the high BIT and the low  $\#rings_{tetra}$  for the Ceará Rise sediments are more promising for brGDGT paleothermometry. However, the trends in brGDGT-derived temperatures seem inconsistent, particularly the absence of any cooling trend over the Plio-Pleistocene transition. Strikingly, the brGDGTs in the Ceará rise sediments are dominated by 6-methyl isomers, resulting in high values (~0.8) for the isomer ratio (IR), whereas

the generally acidic soils in the Amazon catchment mostly contain 5-methyl brGDGTs and are characterised by low IR values. Subsequent comparison of the brGDGT composition in the Ceará rise sediments with that in modern suspended particulate matter (SPM) from the Amazon River demonstrated that the majority of the brGDGTs in the Ceará Rise sediments must have been produced in situ in the river itself. Thus, the Ceará Rise site is also deemed unsuitable for brGDGT paleothermometry.

Finally, the brGDGTs in the Hank borehole seem more promising for paleotemperature reconstruction. Using the  $\#rings_{tetra}$  index, a mixing model, and a newly developed coastal marine transfer function, we could correct the brGDGT record for a marine overprint. This resulted in the first reliable terrestrial MAT record for Pliocene North Western Europe (Dearing Crampton-Flood et al., 2018). To further increase the value of this record for climate modelling, we constructed a high-resolution age model for the Pliocene North Sea basin. This is challenging as coastal settings represent dynamic sedimentary systems with potential lowstand hiatuses, varying freshwater input, and re-transportation, that hampers the straightforward age model construction technique using the stable oxygen isotope ( $\delta^{18}O$ ) signature of benthic foraminifera for tuning to a global  $\delta^{18}O$  reference curve (eg. Lisiecki and Raymo, 2005). We circumvent these issues by an integrated seismo-stratigraphic approach in which we use  $\delta^{18}O$  of endobenthic foraminifera that are less sensitive to freshwater input and re-transportation, resulting in detailed age model for the period ca. 3.2-2.8 Ma. This allows us to place our brGDGT-based temperature record within the mPWP. A marine and terrestrial palynological dataset for the same borehole supports the trends of the MAT record.

Hence, we present the first continuous, well-dated temperature record for continental NW Europe during the Pliocene. Our final record shows that terrestrial temperatures during the mPWP were relatively stable and ranged from 10-12 °C. This is 1-3 °C warmer than the present MAT of the Netherlands. The outcomes of this study also stress the importance of understanding sources of brGDGTs in sedimentary archives prior to applying the brGDGT paleothermometer.

## References

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# Decline of $PCO_2$ from the Miocene based on the $\delta^{13}C$ of algal biomarkers

Caitlyn R Witkowski<sup>1,2\*</sup>, Anna S von der Heydt<sup>3,4</sup>, Marcel TJ van der Meer<sup>2</sup>, Jaap S Sinninghe Damsté<sup>2,5</sup>, Stefan Schouten<sup>2,5</sup>

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Past analogues of likely near-future climate conditions, such as the relatively warmer Middle Miocene Climatic Optimum between 17 and 15 Ma, may help us better understand the current unprecedented rise of carbon dioxide concentrations ( $PCO_2$ ) and its relationship to rising global temperatures. Although temperatures are relatively well-constrained over the past 17 Ma, the evolution of Middle Miocene  $PCO_2$  remains highly uncertain among various proxies. Here we test the proxy potential of the stable carbon isotopic composition of different algal biomarkers, i.e. steranes, phytane, and C37 alkenones, from sediments off the coast of California over this period. From 16.4 Ma to 0.1 Ma, the sterane- and phytane-based reconstructions show a steady decline in  $PCO_2$  from ca. 500-580  $\mu\text{atm}$  to ca. 300  $\mu\text{atm}$ . The alkenone-based  $PCO_2$  record is limited to the final 4 Ma in this sedimentary sequence, but likewise shows similar values and trends. The similarity in values among these disparately produced compounds suggest that general biomarkers may have promise for climate reconstructions. Furthermore, these  $PCO_2$  estimations here mirror global temperature reconstructions, suggesting that  $PCO_2$  and temperature were coupled during this time period.

# Mapping of pigment remnants in fossils

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<sup>1</sup>University of Manchester; <sup>2</sup>College of Charleston; <sup>3</sup>Stanford Synchrotron Radiation Lightsource; <sup>4</sup>Stanford PULSE Institute; <sup>5</sup>Children's Museum of Indianapolis; <sup>6</sup>University of Southampton; <sup>7</sup>Linac Coherent Light Source; <sup>8</sup>Diamond Light Source; <sup>9</sup>Ujita Health University.  
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Determining the pigmentation of extinct organisms is one of the key challenges in paleontology and advances in the analysis of soft tissue has provided great progress. Novel, non-destructive, chemical imaging and spectroscopy techniques, e.g. Synchrotron Rapid Scanning - X-Ray Fluorescence (SRS-XRF) imaging combined with X-ray absorption spectroscopy, has provided new information concerning the distribution of eumelanin residue in fossils (Edwards et al., 2014; 2016; Wogelius et al., 2011). Eumelanin produces dark black/brown colours in (in)vertebrates but is only one of the critical pigments governing colour in these lifeforms. Less is known about the pheomelanin pigment responsible for the lighter reddish-brown colours. Determining the presence of eumelanin was possible since Cu is the metal co-factor in the enzymatic process during its formation (Hearing and Tsukamoto 1991), and elevated concentrations of organically bound copper can be correlated with eumelanin rich fossil tissue (Wogelius et al., 2011). Zinc, the second most abundant metal in mammal melanosomes, may correlate with pheomelanin. In addition, pheomelanin synthesis requires the sulfur containing amino acid cysteine as a substrate, suggesting that there is sulfur contained within the organic units to which Zinc could attach. Indeed, recent analyses of extant pheomelanin-rich feathers indicated a distinct chemical signature for zinc and organic sulfur, with a significant portion of the zinc bound to sulfur, likely through the sulfur contained within the pheomelanin molecule (Edwards et al., 2016). Here, we aimed to test whether pheomelanin can now be mapped in fossils.

Fossil analyses indicate that the zinc coordination chemistry is comparable to that within modern pheomelanin-pigmented hair with similar zinc-sulfur coordination chemistry and zinc-organosulfur compound distribution patterns. Sulfur spectroscopy of modern samples revealed discrete signatures caused by heterocyclic sulfur compounds that could be used as biomarkers for the presence of pheomelanin in fossils. However, the presence of other high-sulfur containing moieties, such as keratinous tissue can cause complications. Oxidising of the disulfide bonds in keratin result in an increased background in the sulfur K-edge spectra obscuring the weaker diagnostic sulfur signatures. This means that sulfur spectroscopy alone cannot be used to map pheomelanin in fossils. However, analyses indicate that the pheomelanin zinc-sulfur bond is more stable than the keratin disulfide bond. Results show the presence of a significant amount of residual zinc-organosulfur compounds despite degradation of the surrounding keratin. Using a combination of organic sulfur XRF mapping and zinc spectroscopy we were able to map the distribution of zinc complexes in fossils. Considering that these complexes are derived from pheomelanin residues, it was possible for the first time to map the distribution of this pigment. This means that the spatial distribution of the different forms of melanin residues in extinct organisms may be resolved non-destructively even after millions of years of degradation. This will not only help us to understand what these extinct organisms really looked like but will also enhance our understanding of how these biomolecules have been preserved over time.

Edwards et al. (2014) *Pigment Cell and Melanoma Research* 27, 684-685; Edwards et al. (2016) *Scientific Reports* 6, 34002; Hearing and Tsukamoto (1991) *FASEB. J.* 5, 2902-2909; Wogelius et al. (2011) *Science* 333, 1622-1626.

# The impact of environmental parameters on the adsorption of azo dyes on Nyex™

Katrina Cullen<sup>1</sup>, Hassan Almoshwer<sup>1</sup>, Daniel Rusev<sup>1</sup>, Fateha Siddika<sup>1</sup>, Yishu Cai<sup>1</sup>, Stephen Boulton<sup>1</sup>, Nigel W. Brown<sup>2</sup>, Mohammed A. Nabeerasool<sup>2</sup>, David Polya<sup>1</sup>, Roy Wogelius<sup>1</sup>, Bart van Dongen<sup>1</sup>

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Clean drinking water is a basic human right; yet 844 million people still lack access to improved water sources (WHO & UNICEF, 2017). In the UK the Drinking Water Inspectorate requires water suppliers to remove all organic contaminants that are present in concentrations above set limits or alter the colour, taste or content of water. This represents a real challenge for the water industry as some compounds are persistent in water or cannot be removed by current technologies/treatment methods.

Arvia Technology Ltd recently developed a novel water treatment technology, which makes use of an adsorption and electrochemical regeneration process, to remove and completely oxidize organic contaminants from aqueous solutions. This process uses a low capacity, proprietary graphitic adsorbent material (Nyex™) that can be electrochemically regenerated. It has been successfully applied in the removal of metaldehyde (Nabeerasool et al., 2015), acid violet (Asghar et al., 2013) and azo dyes (Ravel et al., in prep.) showing the potential to remove a wide range of organic contaminants.

However, there has been little direct comparison between the different types of Nyex™ currently available, e.g. flake and granular Nyex™. Until now the main focus has been on determining treatability rates of specific organic compounds with either type of Nyex™. In addition, little is known about the effects of environmental parameters such as solution temperature, pH and conductivity/dissolved salts on the treatment process. This is important to better understand and predict treatment of real and complex water matrices. In this study model azo dyes (methyl orange & janus green b) are used to determine the impact that different environmental parameters have on the adsorption of dyes onto both types of Nyex™. Adsorption experiments indicate that solution temperature, pH and increased salinity can change the amount of dye adsorbed in 30 minutes, suggesting that environmental parameters do have an impact and need to be considered during the treatment process.

**Keywords:** Nyex™, Arvia, Azo dyes, Water Treatment, Adsorption, Environmental parameters

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# Lichen biomonitoring to assess spatial variability of airborne polycyclic aromatic hydrocarbons (PAHs) in Manchester, UK

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Urban atmospheric pollution and poor air quality is linked to severe health impacts, i.e. respiratory and cardiovascular diseases and cancer<sup>1</sup>. For instance, polycyclic aromatic hydrocarbons (PAHs), produced by incomplete combustion and pyrolysis of organic matter, are considered ubiquitous, persistent, highly liposoluble, semi-volatile, highly carcinogenic and mutagenic toxic compounds regarding human health<sup>2</sup>.

Automated air quality monitoring stations in Manchester, i.e. on Oxford Road and at Piccadilly Gardens, do not record PAH concentrations. This necessitates the application of additional methods to obtain information on spatial distribution of PAH pollution. Because of their morphology, lichens take up and accumulate nutrients and atmospheric pollutants by dry and wet deposition<sup>3</sup>. Lichens have been proven to be useful biomonitors for atmospheric PAHs and can be used for source apportionment of PAH sources (i.e. combustion sources)<sup>4,5</sup>.

Lichens (*Xanthoria parietina* and *Physcia* spp.) were sampled from 20 sites across Manchester city centre area. Lichen material (0.2 g) was solvent extracted with Dichloromethane (DCM) by ultrasonication, cleaned-up by Solid Phase Extraction (SPE) and subsequently analysed for 16 EPA priority PAHs by *Gas Chromatography Atmospheric Pressure Chemical Ionisation – Tandem Quadrupole – Mass Spectrometry* (GC-APCI-MS/MS; GC: Agilent 7890A, MS: Waters APGC Xevo TQ-XS).

Predominant PAHs in lichens were 4-ring PAHs, with a total concentration ( $\Sigma$ ) of 189.82 ng/g, indicating vehicular emissions as major source of PAHs<sup>4</sup>. High-molecular weight PAHs (5- and 6-ring) are usually associated with particulates<sup>4,5</sup>, with analysed total concentrations ( $\Sigma$ ) of 67.98 ng/g (5-ring) and 46.13 ng/g (6-ring), respectively. Benzo[a]pyrene concentrations, one of the most toxic PAHs<sup>5</sup>, were found between 0.42 ng/g and 4.33 ng/g.

Varying concentrations of PAHs indicate site-specific influences, i.e. from vehicular emissions, and illustrate spatial variability of PAH pollution across Manchester. Higher concentrations of 2- and 3- ring PAHs in lichens were found closer to major roads (e.g. A roads and motorways) and with increasing distances to green spaces, respectively. These findings further indicate traffic-related influences on lichen PAHs and beneficial effects of urban green (i.e. improving air quality).

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# Assessing the impacts of oil contamination on soil microbial community/diversity in the Niger Delta (Nigeria)

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Excessive demand for fossil energy has made crude oil pollution a global environmental challenge. Deliberate and accidental oil spills have polluted large areas of land and water with organic and inorganic toxic substances (Holliger et al., 1997). Expectedly, these contaminants can have significant deleterious effect on the ecosystems (Mitchel and Fingas, 2016). In Nigeria, the consequences of oil spills and its alarming regularity has severely damaged the Niger Delta ecosystem for several decades (UNEP, 2011). So far, it is unclear how wide and deep the oil has penetrated, and there is limited information on the impacts of oil contamination on the microbial community/diversity, as well as on their interactions, since understanding indigenous microbial community is paramount to any successful bioremediation process.

This project therefore aims to determine the impact of oil contamination including the impact of heavy metals originally present in the crude oil from a recent oil spill in Ukpeliede community (Niger Delta area) on the microbial community/diversity at depth, over time. To that purpose, soil/sediments were collected from 4 depths (up to 1m depth) along two transect from the point of origin to outside the contaminated area in the autumn of 2018. The extent of the contamination, including the impact of heavy metals originally present in the crude oil, was determined using a combination of (pyrolysis-) GCMS, X-ray fluorescence (XRF) and X-ray diffraction (XRD) analyses. The abundance and diversity of the microbial community at depth will be determined using DNA profiling and metagenomic analysis.

In this presentation the initial results, confirming the presence of the contamination as well as a reduction of the average pollution with depth will be discussed.

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# Biomarker development and deciphering environmental signals

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In order to apply organic geochemistry to modern problems such as those caused by environmental and climate change, scientists need to contextualise the biomarkers, or molecular fossils, ideally from their source in the precursor organism to their sink in the geological archive that preserves them. I lead the Biomarkers for Environmental and Climate Change Science (BECS) research group, which has been developing proxies from biomarkers to address societally relevant questions about human-induced changes in our environment and culture. My research group works on problems around the globe, from impacts of glacial loss in high alpine regions, to understanding hydrology and ecosystem change in drought prone regions like the North American prairies and on the Tibetan Plateau; we have even extended the use of organic geochemistry into addressing whether the Ancient Mesopotamians drank wine or beer. This talk will touch on all these aspects of how biomarkers can help us understand a changing environment, in addition to showing the latest findings over the last 1,500 years from the alpine regions of the Sierra Nevada National Park in southern Spain. The record shows that this vulnerable ecosystem is experiencing stresses imposed by modern climate change and our calibrated algal lipids extend alpine temperatures back 1,500 years. These results highlight the enhanced effect of greenhouse gases on temperature during the last ~200 years and pinpoint the timing for when temperatures began to exceed natural thresholds in the region and the potential reasons why warming rates increased substantially over the last several decades.

The talk will use the drought prone North American prairies as a case study to investigate approaches to developing and applying biomarkers in high resolution lake sediments and explore we are with respect to our understanding of long-chain alkenone, glycerol dialkyl glycerol tetraethers (GDGTs), and long-chain diols, their producers and their relationships with environmental parameters. Here we use a suite of 106 lakes from the Northern Great Plains in Saskatchewan, Canada to develop these biomarkers for palaeoenvironmental reconstructions. We have recently begun ground-truthing our calibrations in short cores from and I will present what we now know about the spatial distribution of biomarkers and how they reconstruct historical climate the region.

# Innovative solutions to extend selectivity and sensitivity of VOC analysis in soils

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The volatile organic compounds (VOCs) in soils stem from a large variety of different sources within soils as soils act as both sources and sinks for these compounds. Many of the VOCs formed in soils are produced by microorganisms living within them. There have been many efforts to fingerprint the VOCs from these complex microbial habitats, most of which are based on the use of solid phase microextraction (SPME). This automated extraction method allows the monitoring of the community structure, physiological state, and activity of any microbial community in a soil without the need of manual extraction or cultivation procedures.

SPME is a fast, economical and solvent-free methodology widely used for the environmental analysis of soils in combination with GC-MS. The methodology using SPME in headspace (HS-SPME) analysis has been used to determine VOCs in a wide range of different soils of varying textures, organic matrices from manures and composts from different origins.

In this work we discuss an innovative mode of extending the sensitivity of SPME extraction called SPME-trap with enrichment in which a refocussing cold trap is used to further pre-concentrate analytes released from a SPME fibre used on soil samples before the analytes are injected into the GC-MS system.

To illustrate the enhanced capabilities of SPME-trap we investigate the fingerprints of VOCs for a soil profile of a loamy and clayey floodplain soils with naturally high groundwater around Llantrisant, UK with a variety of different VOC sample preparation methods showing the benefits of adding high-performance trapping technology to the VOC analysis of soils.

Other techniques used to monitor the VOC fingerprints from soils are static headspace, headspace-or immersive- high capacity sorptive extraction or thermal desorption using sorbent-packed tubes for active or passive, in situ sampling of soil. The focusing trap technology used in this study allows the combination of all these techniques to be run on a single analytical system without the change of hardware. Furthermore, it also allows single and multiple extractions to be carried out automatically on a single sample to increase the analytical sensitivity, thus achieving a comprehensive VOC profile.

# Metabolic Phenotyping of the Soil Microbiome: High Throughput Phospholipid Fatty Acid Analysis of Soils and Sediments

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The soil microbiome is a dynamic ecosystem that responds rapidly to environmental inputs, stresses and changes. It has a significant effect on carbon sequestration, elemental (C, H, N, O, S) flux in the bio-geosphere, nutrient assimilation (and consequently growth) & toxic metal uptake by plants and environmental & agricultural greenhouse gas emissions.

Over the last decade molecular techniques have delivered species level resolution of the soil microbiome however, due to the persistence of DNA in the environment, they offer little temporal resolution and can therefore miss large changes in the makeup of the ecosystem to environmental inputs.

Due to the rapid degradation of phospholipids in the environment, Soil Phospholipid Fatty Acid (PLFA) profiling provides a real-time snapshot of the microbiome structure, with high temporal resolution. As a result, this technique has been widely used for 30 years in the study of soil microbial communities in relation to agriculture, climate change and land management and is highly complementary to molecular techniques.

As the demand for large soil microbiome studies increases to accommodate long-term field and catchment scale studies in agricultural and environmental research, laboratories are facing an increasing workload and demands for higher data quality. Furthermore, classical sample preparation is labour intensive and manual data interpretation require highly skilled analysts. We are currently developing a fully automated solution that combines online, microscale sample preparation and fully automated data analysis, reporting and multivariate statistical analysis for PLFA metabolic phenotyping for soil microbiome studies.

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# Investigating the role of mineral ratio in organic matter preservation in marine sediments

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Burial and preservation of organic matter within marine sediments, especially along continental margins, is an important part of the global carbon cycle, leading to the removal of carbon from the atmosphere over geologically significant time scales [1-4]. An accurate understanding of this cycle is important to allow for more accurate predictions of the effect current elevated CO<sub>2</sub> levels will have [1, 5, 6]. However, despite this critical role, there is still a limited understanding of the mechanisms behind organic matter preservation in marine sediments [1]. Previous studies have identified oxygen availability, the nature of the organic matter and rate of sediment accumulation as important factors in organic matter preservation [2, 3, 7, 8]. However interactions with minerals are considered of particular importance [4]. This is evident from the fact that within marine sediments organic matter content is positively correlated to mineral surface area, and over 80% of organic matter in sediments inseparable from the mineral mass by density flotation [3, 4, 9-16]. However there are still a number of factors that can effect organic matter: mineral interactions. As well as its surface area, type of mineral effects its organic matter binding capacity, with clay minerals and iron oxides being of greatest importance [17]. The nature of the organic matter is also important; with carbohydrates, phosphates and nitrogen containing compounds found to interact more strongly [18-22]. Environmental conditions, such as pH, ionic strength and ionic composition, have also been found to effect the sorption process [23-27]. Despite these many interacting factors previous work has shown a ratio of 1.5 mgCm<sup>-2</sup> of organic matter is commonly found in marine sediments[14]. It has been shown that this is not due to a uniform coating of organic matter, as the organic matter has been observed to be present in discrete areas [10, 12]. In order to investigate this link between organic matter and mineral surface area, I will present results investigating the interactions between different organic matter types, both individually and combined, with the clay mineral kaolinite. Kaolinite was chosen as a clay mineral which is common within the marine environment and the organic matter was chosen to represent different functional groups [28]. These results demonstrate how different organic matters interact with both the mineral and each other resulting in different organic matter mineral ratios.

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# Exploring alkenone calibration and micrometre scale molecular stratigraphy in the Northern Great Plains, Canada

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The Northern Great Plains, Canada's largest agricultural region, is characterised by strong seasonality, exceedance of evaporation over precipitation, and extreme hydrological events (e.g. droughts and floods) [1-3]. Understanding and quantifying the processes that shape the extreme climate in this region is imperative, not only for global climate projections but also as an essential step to mitigate crop loss and to sustain livestock [4, 5].

Quantitative temperature reconstructions using long-chain alkenones have a great potential to provide a better understanding of climate processes in this region [6, 7]. Previous studies have shown a robust relationship between specific alkenones indices and SST in marine systems [8-12]. Subsequent analysis of culture experiments on lake isolates from the Canadian Prairies clearly shows their suitability as a quantitative temperature proxy in terrestrial environments, as well [13].

This research aims to conduct lake-specific, in-situ proxy calibrations and high-resolution (interannual) quantitative palaeoclimate reconstructions during the Holocene Climatic Optimum with cross-validation with independent and calibrated XRF-based proxies on Lake Success (Saskatchewan, Canada) cores.

Here, we present the current progress on these aims with new insights into 1) the performance of established and novel alkenone indices in a saline lake; 2) the potential of MSi technology [14-15] for ultrahigh resolution (ENSO-scale) reconstructions and 3) how we will use that approach in unison with microfacies studies and calibrated  $\mu$ -XRF analyses to get a better understanding on the seasonality of alkenone and element deposition.

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# Microbial carbon cycling in the deep terrestrial subsurface

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The deep terrestrial subsurface hosts a substantial fraction of the Earth's biomass in the form of microbial life, yet accessing these ecosystems is extremely challenging. Shale gas extraction by means of hydraulic fracturing (HF) offers a window into the deep subsurface, and is known to create new microbial ecosystems at a depth of several kilometres [1]. Hydraulic fracturing involves high-pressure injection of water-based fluids kilometres below the surface to fracture shale formations and recover natural gas. Studying the geochemistry and microbiology of HF flowback and produced waters offers a unique opportunity to understand microbial survival in, and adaptation to, the extreme conditions of this deep subsurface ecosystem [2].

We employed geochemical and genome-resolved metagenomic approaches to probe the microbiology of produced waters from a hydraulically fractured shale well in the Marcellus region of the US. We present evidence that the microbial community present in fractured shale is driven by organic carbon in the input fluids. We discovered a novel genus of bacteria, *Candidatus Marcellius*, the genome of which is enriched in polysaccharide-degrading genes, as well as genes implicated in the degradation of common fracturing fluid polymers. This novel organism also has the capacity to withstand the brine-level salinities and viral predation common to these extreme environments.

Combined geochemical and genomic approaches offer a powerful toolkit to study these deep subsurface ecosystems. However, it is extremely challenging to study the microbial processes at play *in situ*, and we are restricted to comparing input and output fluids from engineering operations. The next step in unpicking the drivers of carbon-driven microbial metabolism is to simulate fractured shales in the laboratory. Ambitious plans to achieve this are underway, and results from geochemical and microbiological approaches will allow us to resolve what contribution (if any) the shale organic matter and sulfur content are fuelling microbial metabolism in this manmade extreme ecosystem. Greater understanding of the microbial communities in these environments has far-reaching implications, from reducing environmental impact of shale gas extraction to better understanding the potential for microbial life beyond Earth.

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# Hydrous pyrolysis transformation of methyl-bacteriohopanepolyols to methyl-hopanes and implications for environmental reconstructions

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Bacteriohopanepolyols (BHPs) are the precursors to hopanes, and are used as biomarkers for specific environmental processes and microbial communities. While much of the BHP functionality is lost during the transformation from BHP to hopane, methylation at the C-2 and C-3 positions appear to be retained. This has allowed for use of 2Me-hopanes and 3Me-hopanes (along with other indicators) as biomarkers for paleoenvironments, particularly in petroleum research. However, the extent of conversion of methylated vs nonmethylated BHPs to hopanes has not been fully ascertained, nor has it been measured in environmental samples. We investigated the hopanoids of modern sabkha-associated microbial mats along the Abu Dhabi coastline, a potential depositional analogue for some source rocks within the Jurassic petroleum system. We used high-performance liquid chromatography coupled to positive ion atmospheric pressure chemical ionisation mass spectrometry (HPLC/APCI-MS) to measure two ratios in these samples in order to evaluate the relative abundances of methyl- to non-methyl BHPs: 2MeBHPs/(2MeBHPs + non-methylated BHPs) and 3MeBHPs/(3MeBHPs + non-methylated BHPs). The BHPs measured were bacteriohopanetetrol (BHT), aminotriol, 3Me-aminotriol and anhydroBHT. Approximately 30-40% of the measured BHPs were 3MeBHPs. No 2MeBHPs were observed. Following hydrous pyrolysis of modern mat surface samples, we measured methyl-hopanes by gas chromatography-triple quadrupole mass spectrometry (GC-MS/MS). It was observed that the ratio of 3-methylated hopanes to their respective non-methylated hopanes in the pyrolysates was lower than those in the BHPs in the unpyrolysed samples. This suggests a different transformation rate for either amino- and alcohol-BHPs, or for methylated- and nonmethylated-BHPs. The hopanes of the modern sabkha pyrolysates contained 3Me-hopanes ( $C_{31}\text{-}3\beta\text{-methylhopane} / (C_{31}\text{-}3\beta\text{-methylhopane} + C_{30}\text{-}\alpha\beta\text{-hopane} \sim 3\text{-}7\%)$ ), but the 2Me-hopanes were below detection limits ( $C_{32}\text{-}2\alpha\text{-methylhopane} / (C_{32}\text{-}2\alpha\text{-methylhopane} + C_{31}\text{-}\alpha\beta\text{-hopane} < 1\%$ ). The hopane distributions in the reservoir oil from the Jurassic Arab Formation contained similar levels of 3Me-hopanes ( $\sim 3\%$ ) and more 2Me-hopanes ( $\sim 11\%$ ). This suggests that the present-day microbial community and/or the environmental context of the modern sabkha-surface mats is not consistent with the depositional setting of the petroleum source rock for the Abu Dhabi crude oil.

# $\delta^{13}\text{C}$ values of bacterial hopanoids and leaf waxes as tracers for methanotrophy in peatlands

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Wetlands are the largest natural source of atmospheric methane and play an essential role in the global carbon cycle. The stable carbon isotopic composition ( $\delta^{13}\text{C}$ ) of bacterial and plant lipids has been used to study modern and past peatland biogeochemistry, especially methane cycling. However, the small number of recent peatlands that have been characterised and the lack of consistency between target compounds means that this approach lacks a rigorous framework. Here, we undertake a survey of bacterial and plant lipid  $\delta^{13}\text{C}$  values in peatlands from different geographic regions, spanning a wide range of temperature (-8 to 27°C) and pH (~3 to 8), to generate a reference dataset and to probe drivers of isotopic variability. Within our dataset, the carbon fixation pathway predominantly determines leaf wax (*n*-alkane)  $\delta^{13}\text{C}$  values. Bacterial-derived C<sub>31</sub> hopane  $\delta^{13}\text{C}$  values track those of leaf waxes but are relatively enriched (0 to 10‰), indicating a heterotrophic ecology and preferential consumption of <sup>13</sup>C-enriched substrates (e.g. carbohydrates). In contrast,  $\leq$  C<sub>30</sub> hopanoids can be strongly <sup>13</sup>C-depleted and indicate the incorporation of isotopically light methane into the bacterial community, especially at near neutral pH (~5-6 pH). Previous analysis of Eocene sediments has suggested isotopic decoupling between C<sub>31</sub> and  $\leq$  C<sub>30</sub> hopanoid  $\delta^{13}\text{C}$  values. Our work suggests a profound and globally widespread decoupling in recent peatlands; this persists despite the profound diversity of hopanoid producing bacteria and associated controls on their  $\delta^{13}\text{C}$  values and it has significant implications for future work. Re-analysis of published data from: 1) the (mid-to-early) Holocene and 2) latest Paleocene/earliest Eocene in this revised context highlights that perturbations to the peatland methane cycle occurred during the past, and we envisage that this approach could provide unique (qualitative) insights into methane cycling dynamics throughout the geological record.

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## GDGTs and BHPs in glacial lakes from Northeastern Greenland

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Greenland contains the second largest ice sheet on Earth which covers 80% of the island. The ice sheet contributes to moderating Earth's climate. However, Northeastern Greenland is warming at twice the global average rate, causing the ice sheet to melt and global sea levels to rise. This leads to permafrost thawing and glacial retreat. There is major concern regarding the release of large volumes of meltwater, greenhouse gases, and the potential positive feedback on climate change.

Lake sediments within the glacial-fluvial system contain detailed records of ecosystem change over time, enabling long-term monitoring of sediment flux, vegetation development, microbial community change and mean annual air temperature. Sediment piston cores were collected from Lake 10 in the Zackenberg area, Northeastern Greenland (Figure 1), downstream of a small glacier close to the Greenland Ice Sheet margin. Based on local radiocarbon (<sup>14</sup>C) ages, the sediments span the last c. 2,000 years varying in consistency and texture with depth. Upper sediments are sand-rich, whereas, the lower part of the core consists of clay and silt.

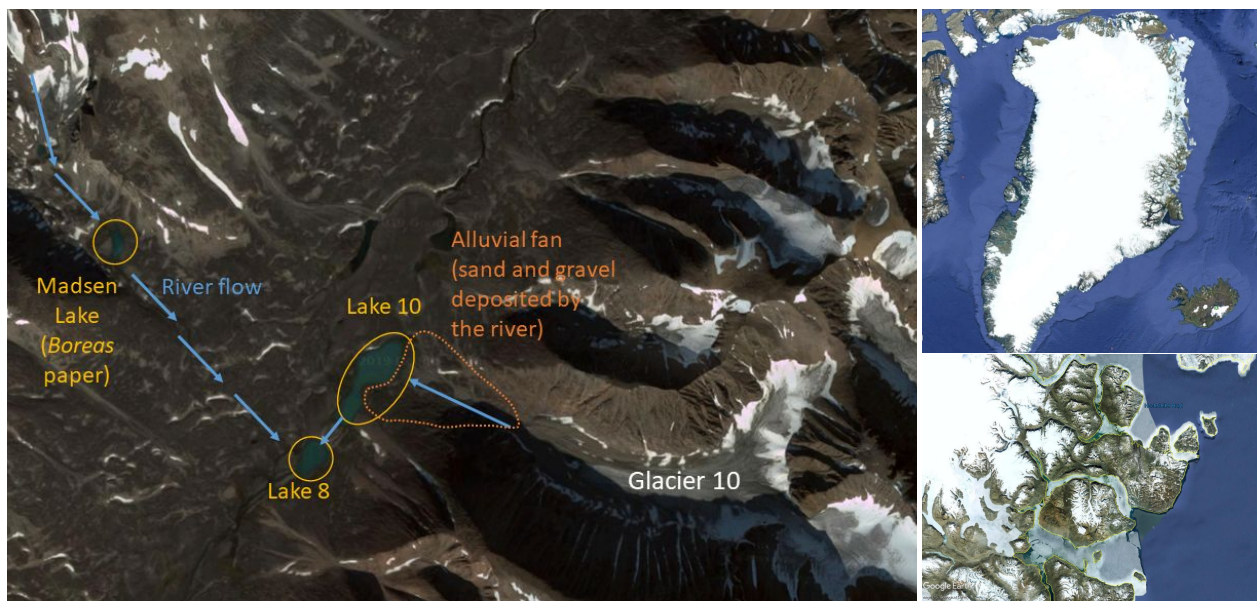


Figure 1: Location of Lake 10 within the Zackenberg Valley, Greenland

Biomarker molecules, including glycerol dialkyl glycerol tetraethers (GDGTs) and bacteriohopanepolyols (BHPs), were extracted from selected core layers using a DCM:MeOH:H<sub>2</sub>O ultrasonic extraction and purified using column chromatography. They will be quantified using LC-APCI-TOF-MS, and the results will provide novel and important data regarding the environmental history of this highly sensitive Arctic region.

# Effect of Weathering on Markers used in Oil Fingerprinting

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Chemical fingerprinting of crude oils and petroleum products is an important technique in environmental forensic investigations. However, its significance is not limited to environmental contamination assessment alone, it is also used in environmental litigation. Due to the environmental impact of petroleum spills, there is need to understand the fate of crude oil hydrocarbons in the environment for forensic purposes for blame apportionment and, for contingency planning, during environmental clean-up and restoration. Once petroleum hydrocarbons are spilled in the environment, they are gradually subjected to increased dispersion and degradation processes, collectively termed weathering. This work investigates the effects on molecular markers of the main weathering processes including evaporation, water washing, aerobic and anaerobic biodegradation and, focused on biomarkers in two crude oils (light and medium) from the Niger Delta region of Nigeria and from the North Sea. Chromatographic data was obtained from crude oil evaporation experiments using gas chromatography/mass spectrometry (GC/MS) in accordance with the Nordtest methodology of fingerprinting (Daling et al., 2002). Biomarkers were evaluated as the more degradation-resistant hydrocarbons in petroleum in the environment, amongst other groups such as *n*-alkanes, isoprenoids, and aromatic hydrocarbons (e.g. Wang et al., 2006). Data showing the effect of evaporation on a range of molecular markers including hopanes, steranes, bicyclic sesquiterpanes and diamondoids will be presented. Novel sesquiterpanes were identified in the two Nigerian crudes and the extent of their resistance to weathering will be discussed in terms of their potential for use as markers for forensic and correlation purposes.

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# The Development of 3-Hydroxy Fatty Acid-Based Palaeoclimate Proxies

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C<sub>10</sub>-C<sub>18</sub> 3-hydroxy fatty acids (3-OH FAs) are diagnostic biomarkers for Gram-negative bacteria and are commonly found in modern terrestrial and marine settings. The recent proposal of novel 3-OH FA-based palaeoclimate indices comprising RAN<sub>15</sub> and RAN<sub>17</sub> for temperature reconstruction and RIAN, RIN and the Branched Index for reconstruction of soil pH (Wang, et al., 2016), has led to the further exploration of these proxies in localised environmental transects (Huguet, et al., 2019). Most recently these proxies were used to reconstruct the first independent, biomarker based, temperature and hydrological signals from the HS4 stalagmite in central China (Wang, et al., 2018). However, the continental-scale spatial performance of 3-OH FA-based palaeoclimate proxies in the terrestrial realm remains unexplored. This study reports the first 3-OH FA-based palaeoclimate indices from a continental-scale soil transect along the US East Coast, a latitudinal transect with a natural temperature gradient ranging between 7 and 23°C. 3-OH FAs were extracted from 12 soil samples collected between Maine and Florida, and underwent subsequent analysis by GC-MS. Both RAN indices displayed significant correlations with MAAT ( $R^2 = 0.51-0.62$ ,  $p < 0.01$ ), whereby the proportion of *anteiso*-C<sub>15</sub> and C<sub>17</sub> homologues increased at lower temperatures. Significant correlations of RIAN, RIN, and the Branched Index with soil pH ( $R^2 = 0.49-0.57$ ,  $p < 0.05-0.01$ ) were indicative that the proportion of branched 3-OH FAs increased with soil pH. The 3-OH FA Branching Ratio uniquely correlated with MAAT at sample sites between Connecticut and Florida, where MAAT and soil pH were found to co-vary. Such results are concordant with the homeoviscous adaptation response of Gram-negative bacterial membrane lipids to the external environment, and are analogous to aggregated 3-OH FA indices from Mt Shennongjia (Wang, et al., 2016), Mt Majella, and Mt Rungwe (Huguet, et al., 2019) soil transects (in the respective locations China, Italy, and Tanzania), despite variability in seasonal climatic regime and vegetation cover along the US East Coast. This study thus demonstrates the ability of 3-OH FAs to quantify the physiological response of Gram-negative bacterial membrane lipids to growth temperature and soil pH, and supports the application of 3-OH FAs as a novel terrestrial biomarker.

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# Development and application of novel ecological and environmental proxies from leaf wax lipids

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Plant waxes seal leaf surfaces and form the barrier between the leaf interior and the environment. Their chemical and isotopic composition varies between plant species, and responds to environmental conditions such as temperature, moisture availability and atmospheric carbon dioxide concentration (pCO<sub>2</sub>) in systematic and potentially predictable ways. On leaf death, waxes dissociate from the leaf surface and enter soils and sediments. Due to their excellent preservation potential, leaf wax lipids are preserved in the geologic record, where they provide an archive of biological information from which we can extrapolate the environmental conditions at the time of their formation. If these relationships can be quantified in the modern, they allow reconstruction of plant responses to climate forcing. Of particular interest are shifts in the isotopic composition of leaf waxes in response to changes in atmospheric pCO<sub>2</sub>. We intend to test these relationships between environment and wax composition using leaf samples taken from the BIFoR Free Air CO<sub>2</sub> Enrichment (FACE) experiment's enhanced pCO<sub>2</sub> woodland, as well as growth chamber experiments. Results will show the value of leaf wax lipids as proxies for past climate change, and provide insights into plant response to future anthropogenic climate forcing.

# Assessing organic and heavy metal pollution in post-industrial Manchester

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Soil samples from four sites around Manchester were tested for polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs). PAHs can have multiple short- and long-term health effects including cancers and skin irritation. HMs have wide-ranging health effects including organ failure, nerve system damage, and cancers. PAHs were extracted via hexane solvent extraction, with a biphenyl internal standard, separated using aminopropyl SPE cartridges, and measured using GC-MS, while HMs were extracted using a concentrated nitric acid digest and measured using ICP-OES. Measured PAH and HM concentrations were then compared to limits from governmental regulations within the European Union (EU).

Both historical and current activities may have contributed to pollution at these sites, and it is thought that pollutants could have been transported downstream by the river Medlock, which runs past all sites.

Medlock Valley (MV) is a non-industrial area upstream of nearby industry, which includes an active sewage works. HM pollution levels were similar across all the sites, with some exceptions. Levels of cadmium in particular were high in MV, with a concentration of almost 1 mg kg<sup>-1</sup>, around double the cadmium levels measured in Clayton Vale (CV) and Philips Park (PP), and around one tenth of the EU limit.

CV has had varied past industrial uses including a hospital, a dye works, and a colliery tip. Indeed, this site turned out to be possibly the most polluted, including showing significant concentrations of a number of PAHs. Just downstream from CV is PP, which showed high levels of copper, zinc, and arsenic, but extremely high levels of lead (around 110% of the EU limit), despite its relatively benign history as a public park since 1846. This highlights the propensity for pollutants to be carried and deposited downstream.

The site furthest downstream was All Saints Park (AS) located on the MMU campus. AS showed relatively high levels of copper, zinc, lead, and arsenic, the reasons for which could be wide-ranging: It is the former site of a church – around 16 000 bodies were buried in the church's burial ground, which was later converted into a playground between 1935 and the 1980s. The church itself was damaged during the Blitz, which could have introduced HM pollution. MMU took over the lease in the 1990s and replaced the top soil, possibly bringing in pollution from an entirely different location. Today, construction sites are located nearby, and a main road has been located next to the site for centuries. Generally, there was a decrease in HM levels downstream, and PAHs were generally seen in low concentrations. Pyrene was a prevalent PAH in every site except for MV.



# Fate of Terrigenous Nitrogen in Arctic Shelf Sediments-An update

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Climate warming in the East Siberian Arctic region has caused an enhanced transport of huge amounts of 'old' terrestrial organic matter, previously stored for thousands of years in the (thawing) Siberian permafrost, to the East Siberian Arctic Seas (ESAS; Vonk et al., 2012). The fate of the organic carbon part of this remobilised terrigenous organic matter is still a matter of debate. However, recent studies indicate that more of this organic carbon is degraded in the Arctic shelf water column and released into the atmosphere than previously thought, particularly close to the point of origin, e.g. river outflow or coastal erosion of organic rich Pleistocene permafrost ice complex deposits Doğrul Selver et al., (2012). This is causing a further positive feedback to global climate warming (van Dongen et al., 2008; Karlsson et al., 2011).

Much less is known about the fate of the terrigenous organic nitrogen, although previous analyses of terrestrial derived dissolved organic nitrogen indicates it to be less degraded if compared to the marine dissolved organic nitrogen, suggesting a (more) conservative behaviour in the Arctic Ocean (Dittmar, Fitznar and Kattner, 2001). Our latest bulk nitrogen analyses ( $\delta^{15}\text{N}$  and organic carbon/nitrogen ratios) show a strong correlation between  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  suggesting a comparable fate for the terrestrial nitrogen and organic carbon in this Arctic region. This indicates a less conservative behaviour than previously thought, e.g. higher potential for diagenetic remineralisation of nitrogen in these sediments, suggesting a potentially larger influence on the  $^{15}\text{N}$  isoscape in Arctic shelf seas and ultimately that of the Arctic Ocean and the Arctic food web. However, these analyses are only done on the bulk level indicating the need for more detailed compound specific (amino acid)  $\delta^{15}\text{N}$  analyses.

This data set has now been expanded to include a larger number of samples analysed from the ESAS and samples from more recent cruises to the Fram Strait and Barents Sea (JR16006 and JR17005).

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# Biomarkers in Stalagmites: Reconstructing Temperature, Hydrology, Vegetation and Bacterial Responses to Climate Change

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## Abstract

Stalagmites have become a key archive in Quaternary palaeoclimatic reconstruction due to their ability to yield continuous and undisturbed records, precise and absolute chronologies, and their global terrestrial distribution. Oxygen isotopes are effectively the master proxy for speleothem analysis, but inherently encode a mix of climatic signals. Thus it is challenging to deconvolve the temperature and precipitation signal from speleothems. Bacterial derived 3-hydroxy fatty acids (3-OH-FAs) have potential as independent temperature and pH proxies.

By applying the 3-OH-FA based temperature proxy RAN<sub>15</sub> and the pH proxy RIAN to the HS4 stalagmite from central China, we recently reconstructed Holocene temperature and hydrological changes, respectively. We now address the issue of how terrestrial carbon storage feeds back on warm climate states, which is critical for improving global warming projections. Soils may act as a positive feedback on climate if warming increases soil carbon decomposition rates. Conversely, if increases in net primary production (NPP) exceed increases in decomposition, the climate feedback will be negative. Here we present new constraints on the response of terrestrial carbon cycle feedbacks, especially soil respiration, during earlier warm episodes of the early Holocene Climate Optimum (HCO) and Medieval Warm Period (MWP), which have hitherto been poorly constrained due to a lack of proxies (and thus available data). We utilize the first palaeoclimatic application of compound-specific  $\delta^{13}\text{C}$  measurements on *n*-fatty acid biomarkers extracted from a stalagmite. We resolve a proportional increase in C<sub>3</sub> plants in the catchment area during these warmer/wetter intervals. Moreover, we find that heterotrophic soil respiration was highly substrate selective, indicating that NPP outpaced decomposition and the catchment behaved as a carbon sink. Thus, we provide the first palaeoclimate evidence that subtropical mineral soils in warmer/wetter climates can act as a negative climate feedback.

# Mid-Pliocene North Atlantic warming: an insight from marine and terrestrial records

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The mid-Pliocene Warm Period (mPWP) (3.025–3.264 Ma) is considered an analogue for 21<sup>st</sup> Century climate change, with similar continental configurations, sunlight intensity and atmospheric CO<sub>2</sub> concentrations to present-day; this short time interval provides a unique insight into global temperature patterns, potential causal mechanisms and enables the prediction of future climatic effects. Dowsett et al. (2013) presented global mPWP Sea Surface Temperature (SST) compilations which indicate enhanced warming in the North Atlantic region, with anomalies of +8°C based on alkenone methods (Robinson, 2008); this magnitude of warming is controversial and far exceeds the conservative SST estimates (a rise of 2–3°C) predicted by the Pliocene Research, Interpretation and Synoptic Mapping (PRISM) reconstructions and leading climate models (HadCM3) (Dowsett et al., 2012). Here, we present new Pliocene U<sup>K</sup><sub>37</sub> SST data enabling us to further examine the extent and duration of North Atlantic warming and evaluate discrepancies between proxy and model estimates. Our pilot alkenone results concur with the magnitude of proxy-based warming previously suggested (Haywood et al., 2016). However we subsequently filtered and corrected our new data to rectify for warm U<sup>K</sup><sub>37</sub> bias caused by low alkenone concentrations (Grimalt et al., 2001). The corrected (and cooler) U<sup>K</sup><sub>37</sub> data indicate the magnitude of warming, in the North Atlantic, may be significantly less (up to 4°C lower) than previously thought, conforming to model predictions. Preliminary branched GDGT temperature estimates from onshore Iceland are also presented to provide greater insight into regional North Atlantic spatial temperature variability during the mid-Pliocene.

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# A New Approach for Studying Past Sea-level Changes Using Molecular Fossils

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Targeted analysis of organic materials in soils is useful for evaluating past environmental conditions, as specific fauna / flora are related to sea-level changes. However, this depends on the preservation of macro and microfossils in the sediment. Specific molecular fossil compounds, termed biomarkers, preserved in the soil matrix, may be directly linked to organisms and hence to the conditions in which they thrived. Variations in biomarker distributions have therefore become a powerful tool for understanding changes in palaeoclimate conditions.

This work determines the utility of molecular fossil marker evidence for Quaternary sea-level changes in sediment deposits from the UK. The cores consisted of unconsolidated immature sediments from the mid-late Pleistocene (< 500,000 years) that represented sea-level transgressions<sup>1,2</sup>. The production of biomarkers, such as chlorophyll pigments and lipids, change as a response to palaeoenvironmental conditions, providing a useful marker for sea-level changes<sup>3-4</sup>. Fluctuations in the pigment and *n*-alkane distribution reflect changes in primary producer activity, while the GDGT-based index of branched and isoprenoid tetraether lipids (BIT) differentiates between terrigenous and marine organic matter inputs<sup>5</sup>. Lipids were analysed by GC-FID and HPLC-MS while analysis of chlorophyll pigments was carried out using a new UHPLC-DAD method. The amino acid racemisation (AAR) chronology provides temporal constraints to the transgressions, enabling the reconstruction of Pleistocene sea-level changes beyond the capabilities of <sup>14</sup>C dating<sup>6</sup>.

The results from biomarker analyses show excellent time-resolved agreement with the lithological and ecological interpretation, but enabled a more sensitive response of different primary producers to changing conditions to be observed. Linking the pigment, lipid and chronological records, the impact of climate change on the primary producer communities and preservation of molecular signatures can therefore be assessed over transgressive phases of sea-level change. This coupled approach enables exploration of a far wider set of sediments for understanding the past.

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# brGDGT Lipid Biomarkers as a Post-Glacial Environmental Proxy

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Continuous detailed records of deglaciation following the last glacial maximum exist in proglacial and post-glacial lake sediment records, offering multiple environmental proxies. This project has extracted such sediments and is applying cutting-edge analytical techniques to reconstruct the environmental conditions present following the retreat of the British and Irish Ice Sheet (BIIS).

One such technique is the use of lipid biomarkers to reconstruct soil pH temperatures. Recent works have highlighted the utility of branched Glycerol Dialkyl Glycerol Tetraether lipid biomarkers (brGDGTs) in temperature and pH reconstructions (Weijers et al., 2007; Tierney, 2012; De Jonge et al., 2013; Hopmans et al., 2016; Naafs, Gallego-Sala, et al., 2017; Naafs, Inglis, et al., 2017).

GDGTs are long chain lipids produced by bacteria and archaea in the formation of cell membranes. GDGTs possess characteristics that can be influenced by environmental factors and thus may be used as proxies for past environmental conditions. These relationships were demonstrated to be applicable to late-glacial/early Holocene through a case study of the Hani Peat Sequence from north-eastern China, with results indicating 3-5 °C warming between the late-glacial and late Holocene (Naafs, et al., 2017).

Samples from the upper section of cores taken from Chat Moss, Salford, UK span the transition from inorganic sands and clays into organic-rich peat following the last deglaciation and proceeding climate amelioration. brGDGTs from these samples have been analysed via LC-MS, and a recently-published temperature calibration applied (Naafs, Inglis, et al., 2017), allowing for a temperature profile over time to be plotted and linked to existing models of glacial retreat and recolonisation in the area. These preliminary results demonstrate the suitability of lipid biomarkers as a paleo-environmental proxy for post-glacial environments and indicate how they present a strong potential to improve our current model of deglaciation in the British Isles.

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# What does lacustrine sedimentary n-alkane average chain length from the Tibetan Plateau tell us?

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## Abstract Text

Long-chain n-alkanes are one of the most common organic compounds in terrestrial plants and well preserved in different natural archives. Because n-alkanes are relatively resistant to degradation, they provide high-fidelity records of past climate and environment changes. Nevertheless, previous studies indicate that n-alkane proxies are region-specific, and require regional calibrations. Even for the same region, temperature or precipitation can have differential controls on the n-alkane average chain length (ACL) and necessitates careful consideration, especially in regions like the Tibetan Plateau (TP) where topography, biome types, and source moisture are highly variable. To further evaluate the impact of climate on ACL for alpine lakes, this study examines the surface sediment n-alkane distributions and concentrations in 55 lakes in the southwest and northeast TP lying along a considerable climate gradient (annual mean precipitation ranges from 25 to 719 mm, temperature ranges from -8.11 to 4.29 °C). We also analyze a short sediment core from a lake in southwestern TP and compared ACL data with local weather conditions. Both core-top and instrumental calibrations aim to answer the following questions: 1) What is the main driver of climate (precipitation and/or temperature) on n-alkane chain length across the TP? 2) Does ACL respond differently between biome types?

## References

# Alternative Approach to the Measurement of Cholesterol and Cholestanols as Signatures of Human Activity in Archaeological Contexts

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## Abstract

Cholesterol and its stanol transformation products (cholestanols) are widely used in soils and sediments as indicators for human activity in archaeology [1, 2]. A limitation to quantifying cholesterol and cholestanols by the conventional method, gas chromatography (GC), results from the low amounts of the analytes in archaeological samples. Hence, strategies for enhancing GC signal response, such as increasing the sample injection volumes and using of splitless injection, are often employed. This work uses a novel derivatising agent for measurement of steroidal alcohols in soils and sediments and demonstrates the application of the method to archaeological soil samples [3]. The good response for the products obtained from derivatisation of a standard of cholesterol reflects the completeness of the derivatisation process (88%,  $n = 7$ ). Chromatographic and mass spectral (MS) characteristics of the derivatives of cholesterol and its stanols have been investigated by ion trap MS. Analysis of the cholesterol and stanol derivatives in archaeological grave soil samples is compared with a conventional derivatising agent, trimethylsilyl ether (TMS). This preliminary evaluation indicates the potential for use of this approach to detect human activity in archaeological contexts with greater security and improved detection limits.

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# Resinous Coating of Takabuti - the Belfast Mummy

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Takabuti, an Egyptian mummy dating back to ~660BC (25<sup>th</sup> dynasty) has been housed by the Ulster Museum in Belfast since 1834, being unwrapped the following year. In the past x-ray and CT scans have been carried out and small samples have been analysed microscopically for disease, hair colour and samples taken for DNA analysis. For the first time GC-MS, TD-GC-MS (thermal desorption) and PY-GC-MS (pyrolysis) have been carried out to determine the compounds used to coat the wrappings during mummification.

Combining the results from all methods, a number of compounds suggesting plant and possibly animal origins can be identified. *n*-alkanoic acids, which are generally found in a variety of oils and fats suggest a plant and/or animal origin. Cholesterol, could suggest a contribution of animal fats, but could also come from the breakdown of the mummy tissues themselves (Brockbals et al., 2018). Small amounts of *n*-alkanols found are also major components of plants. Other acids identified suggest a plant origin; most notable dehydroabiatic acid, 7-oxodehydroabiatic acid, and 15-hydroxy-7-oxodehydroabiatic acid, which are likely to be formed through the dehydration of pine resin (Jones et al., 2014; Menager et al., 2014; Lucejko et al., 2017; Brockbals et al., 2018). The defunctionalised diterpenoid retene, the final stable thermal degradation product of Pinaceae resin tars (Robinson et al. 1987) supports the presence of oxodehydroabiatic acids observed in the TLEs. Ricinoleic acid possibly from the seeds of *Ricinus communis* L. (Euphorbiaceae), has been identified in Egyptian mummy samples (Copley et al., 2005 and Tchaplá et al., 2004) indicating the use of castor oil during the embalming process. Camphor has been identified and can be derived from different plant oils including cedar oil, but cannot be linked to a specific source (Lucejko et al., 2017; Scholz-Böttcher et al., 2013).

Only minor amounts of *n*-alkanes could be detected, indicating an absence of a natural petroleum hydrocarbon (bitumen) source. In addition, other biomarkers generally associated with the presence of bitumen, such as triterpanes/hopanes (*m/z* 191) and steranes (*m/z* 217) could not be detected. The homologous series of *n*-alkane/alkene doublets ranging in carbon number from C<sub>7</sub> to C<sub>34</sub> seen are comparable to those generally observed in pyrograms of fossilised plant/leaf material (Edwards et al. 2011).

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# OPTiMAL: A new machine learning approach for GDGT-based palaeothermometry

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The relative abundances of Glycerol dialkyl glycerol tetraether (GDGTs) compounds produced by modern marine archaeal communities show a significant dependence on the local sea surface temperature at the site of formation. When preserved in ancient marine sediments, the measured abundances of these fossil lipid biomarkers thus have the potential to provide a geological record of long-term variability in sea surface temperatures. Several empirical calibrations have been made between observed GDGT relative abundances in late Holocene core top sediments, forming the basis of the widely used TEX<sub>86</sub> palaeothermometer. There are, however, two outstanding problems with this approach, first the appropriate assignment of uncertainty to estimates of ancient sea surface temperatures based on the relationship of the ancient GDGT assemblage to the modern calibration data set; and second, the problem of making temperature estimates beyond the range of the modern empirical calibrations (>30 °C). Here we apply modern machine-learning tools, including Gaussian Process Emulators and forward modelling, to develop a new mathematical approach we call OPTiMAL (Optimised Palaeothermometry from Tetraethers via **MA**chine Learning) to improve temperature estimation and the representation of uncertainty based on the relationship between ancient GDGT assemblage data and the structure of the modern calibration data set. We provide a new quantitative measure of the distance between an ancient GDGT assemblage and the nearest neighbour within the modern calibration dataset, as a test for significant non-analogue behaviour. We further reduce the root mean square uncertainty on temperature predictions (validated using the modern data set) from  $\sim\pm 6$  °C using TEX<sub>86</sub> based estimators to  $\pm 3.6$  °C using Gaussian Process estimators for temperatures below 30 °C.