Supplementals Datas

Study of the biocrudes obtained via Hydrothermal Liquefaction (HTL) by wild algaes consortium under different conditions

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LDI FTICR MS characterization of bio-oils

Sample Preparation. Samples were solubilized in toluene and further diluted in methanol/toluene (50/50 v/v) to a final concentration of 10^{-5} mg.mL^{-1} for Atmospheric Pressure PhotoIonization (APPI) and 5 mg.mL^{-1} for Laser Desorption Ionization (LDI).

Instrumentation. A hybrid quadrupole FTICR instrument (Solarix XR, Bruker Daltonics, Bremen, Germany) equipped with a 12 T superconducting magnet was operated in the positive laser desorption ionization. For LDI analysis, mass spectra were acquired over a mass range of *m/z* 110-1,300 for 200 scans for broadband experiments. The signal was digitalized with 8 M points resulting in a transient length of 3.4 s. The experimental conditions were set as follows: Octopole energy, 350 Vpp ; quadrupole lower cut-off , *m/z* 150; quadrupole collision energy, 1200 Vpp ; TOF duration, 0.75 ms. Each LDI mass spectrum for each position is the result of 200 consecutive laser shots for a laser power of 18%.

Mass spectrometers were externally *m/z* calibrated using sodium trifluoroacetate solution before sample analyses. Instrument control and data acquisition were provided by DataAnalysis (version 5.0). CERES (self-developed Matlab-based interface) and OriginPro (version 2016) were used to process and visualize the data sets.

From the molecular formulas determined from the accurate mass measurements (errors typically < 0.2 ppm), the number of double bond equivalents (DBE) values were calculated from Equation 1 (c: carbon number; h: hydrogen number; n: nitrogen number) for a molecule with molecular formula $C_cH_hN_nO_oS_s$. Giving a resolving power of 900 000 at *m/z* 400, it is possible to separate class N_1 ions from class N_1S_1 (mass split: 3.4 mDa) compounds.

$$\boldsymbol{DBE = c - \frac{h}{2} + \frac{n}{2} + 1}$$

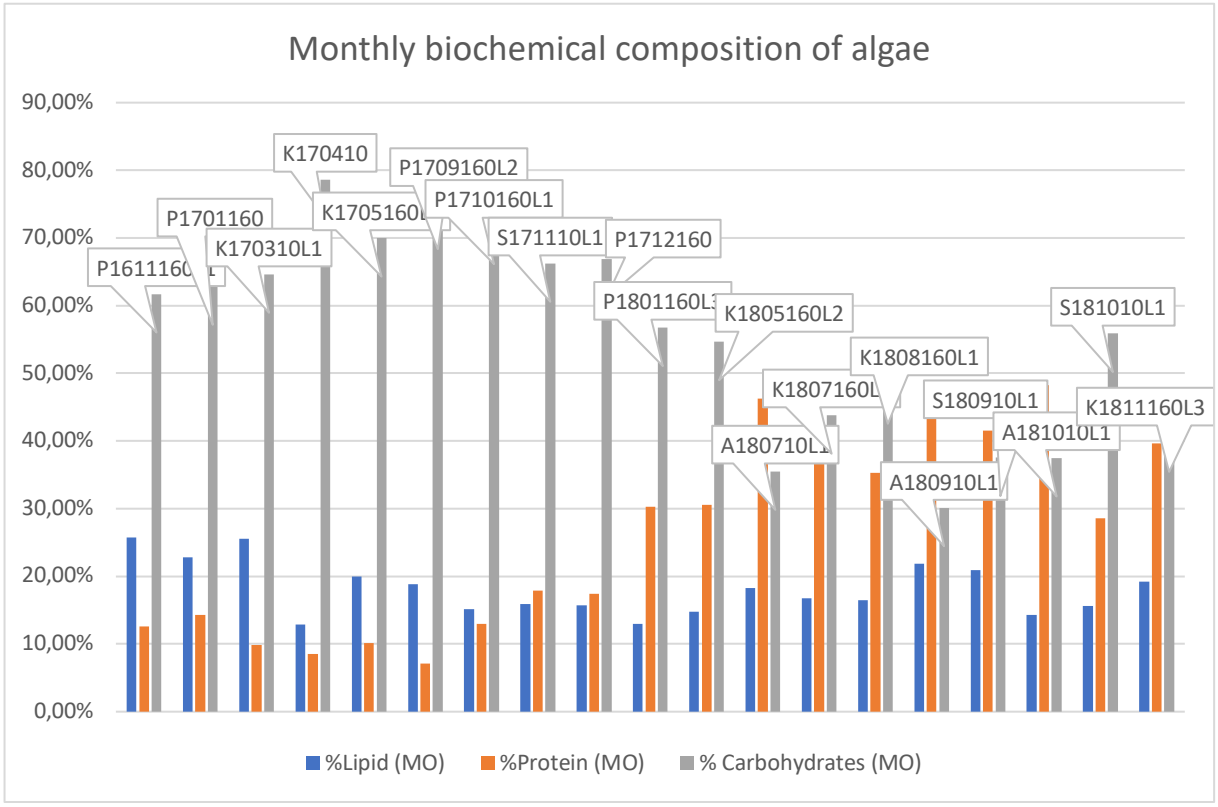


Figure S1. Variation of the biochemical composition of algae batches along the project

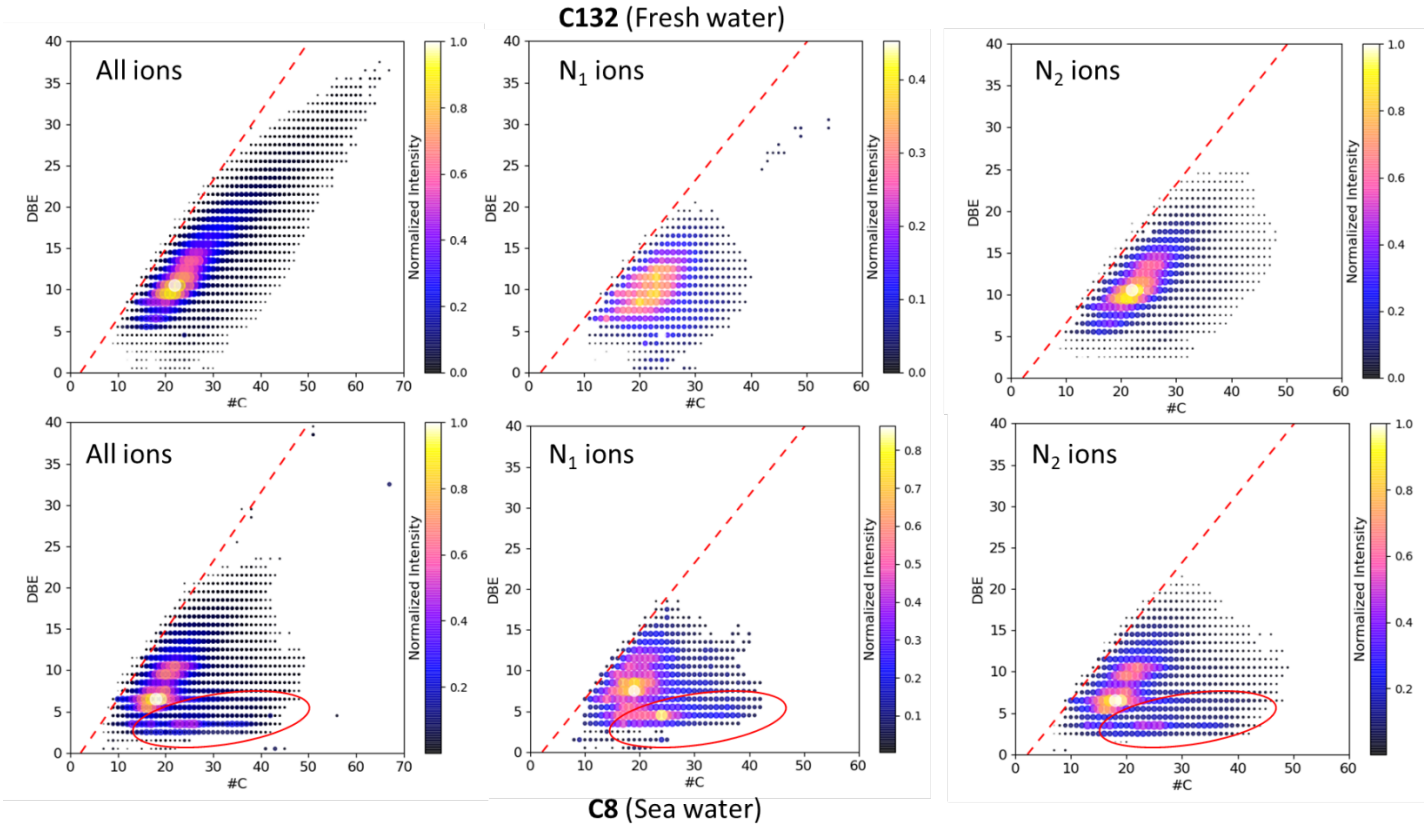
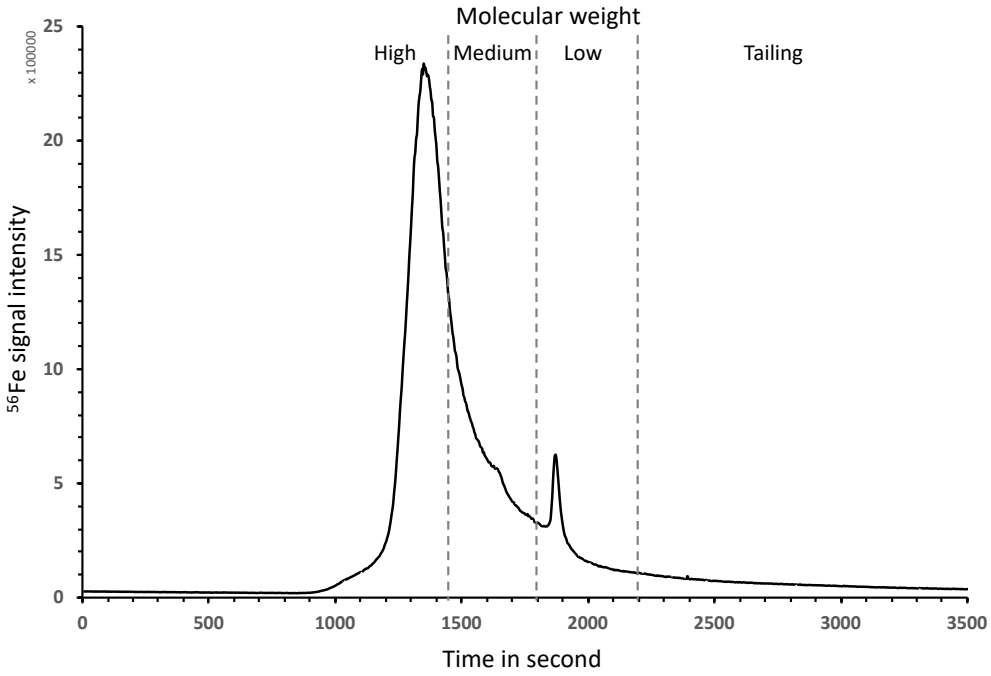


Figure S2. FTICR-MS analysis of two different bio oil C8 and C13-2, respectively coming from sea and freshwater. classes of molecules containing 1 or 2 nitrogen atom (N_1 and N_2) have been represented in DBE vs C number.

a)



b)

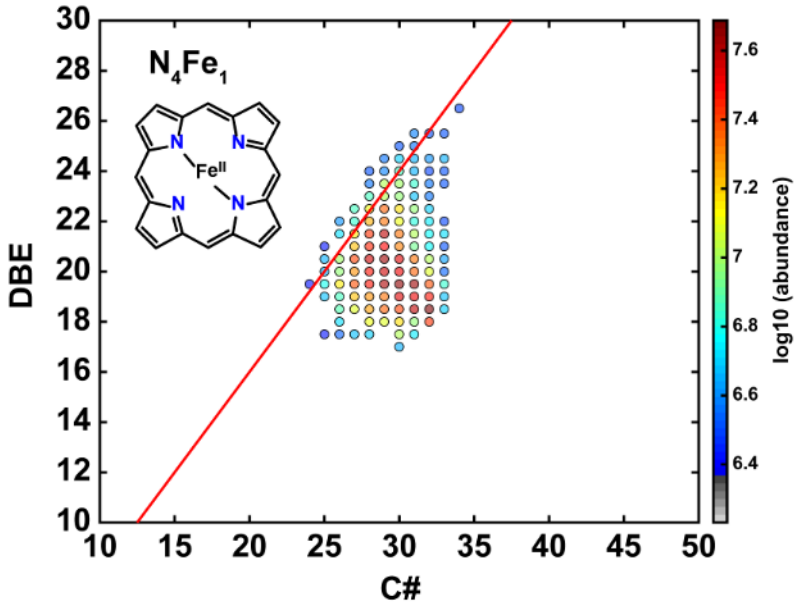


Figure S3. GPC ICP MS a) and DBE/C# map for N_4Fe_1 class detected in LDI+, in the C13-1 bio-oil sample b).