



Molecular Characterization of the Water-Soluble Species Extracted from the Deepwater Horizon Crude by Negative-Ion Electrospray Ionization FT-ICR Mass Spectrometry

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Introduction

On April 20, 2010, an explosion on the Deepwater Horizon (DWH) drilling unit caused the subsequent release of ~5 million barrels of crude oil into the Gulf of Mexico (GOM). Knowledge of the composition of this crude oil is instrumental in determining its fate in the aquatic environment. The GOM has rich and diverse marine fishing reserve and it supports commercial fishing for many communities in the Gulf Coast. Thus, the identification of water-soluble compounds in the crude oil is important so as to determine what components of the crude oil are likely to be of toxicological concern to a variety of aquatic organisms including fish. We applied a known procedure for the extraction of water-soluble species from crude oils.¹ The water-soluble species from the DWH crude oil and the parent crude oil were subsequently characterized at a molecular level by use of negative-ion electrospray ionization (ESI) Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS).

Methods

A liquid-liquid extraction (LLE) was performed on DWH crude oil to extract two water-soluble fractions 1) neutrals & bases and 2) organic acids (see Figure 1). Extracts were dried under N₂ gas until a stable mass was obtained. The DWH crude and its water-soluble extracts were analyzed at the National High Magnetic Field Laboratory by a custom-built 9.4 T FT-ICR mass spectrometer equipped with a micro-electrospray source. Samples were analyzed at a concentration of 250 µg/mL in 50:50 toluene:methanol (v/v) with 0.5% (v/v) tetramethylammonium hydroxide as a modifier in the electrospray solvent system by negative-ion ESI FT-ICR MS. Data were calibrated and processed with a custom software package (PREDATOR).²

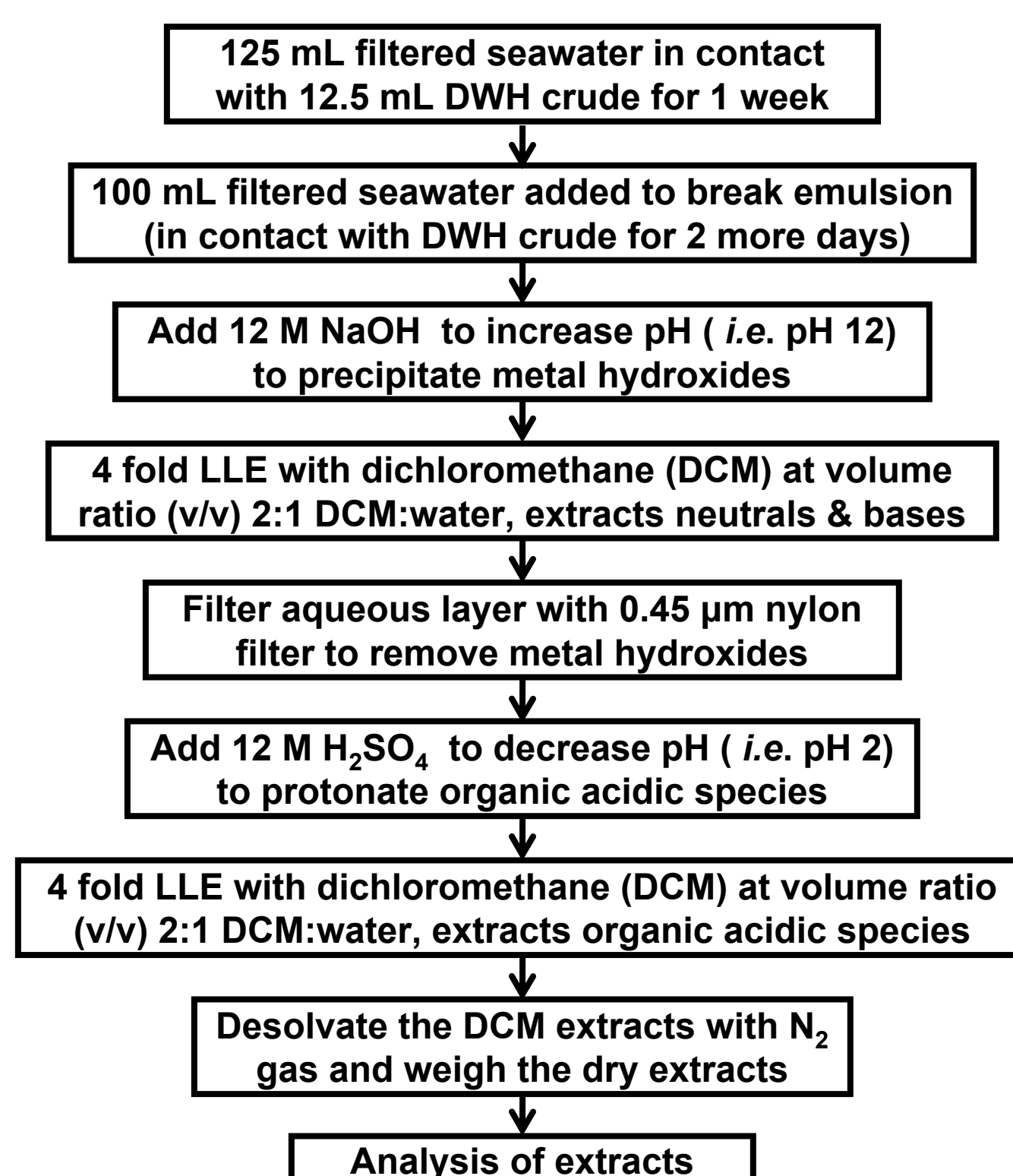
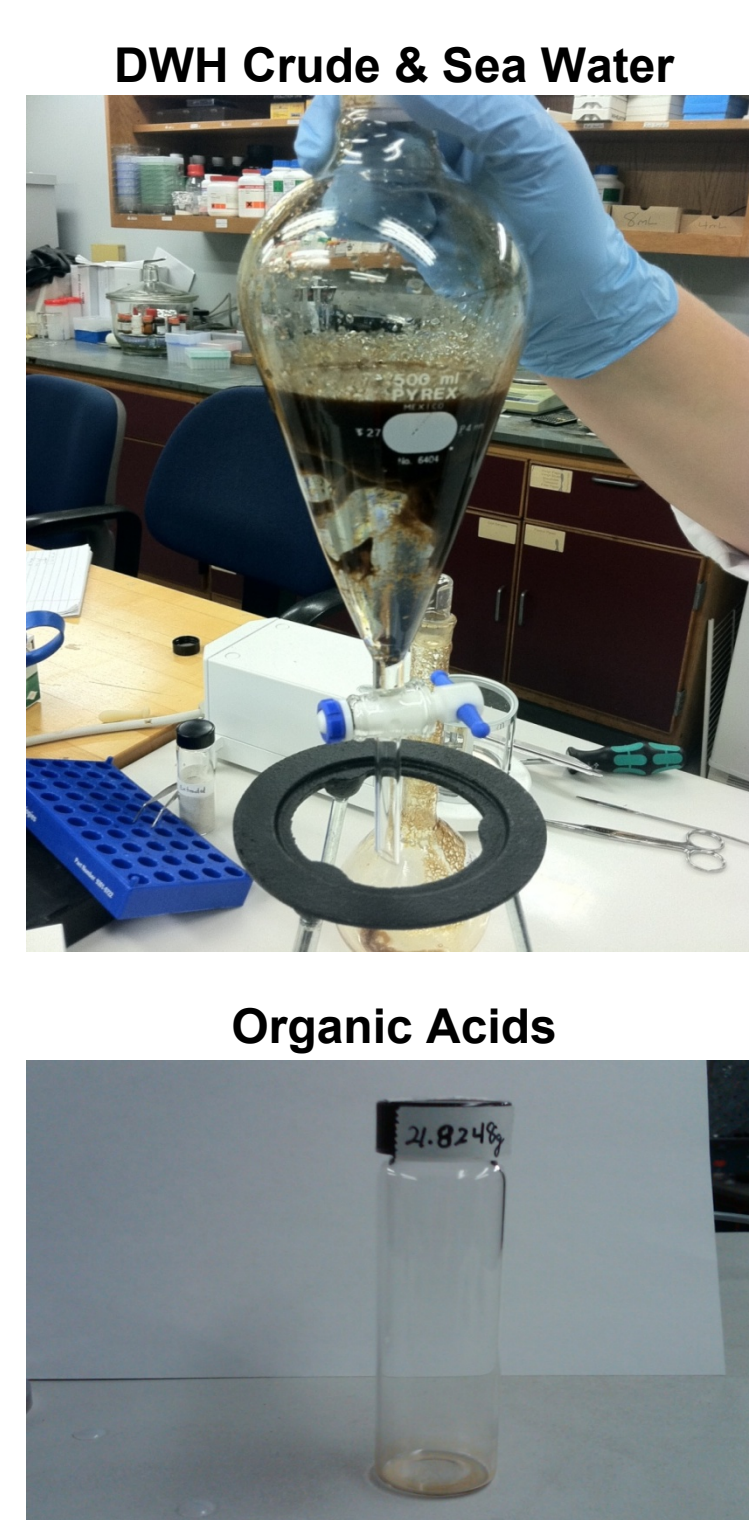


Figure 1. Scheme of a liquid-liquid extraction (LLE) of water-soluble species in a crude oil (right).¹ An emulsion of crude oil and seawater formed in the separation funnel (top left) during a LLE from which we procured the organic acids (bottom left) and neutrals & bases extracts.

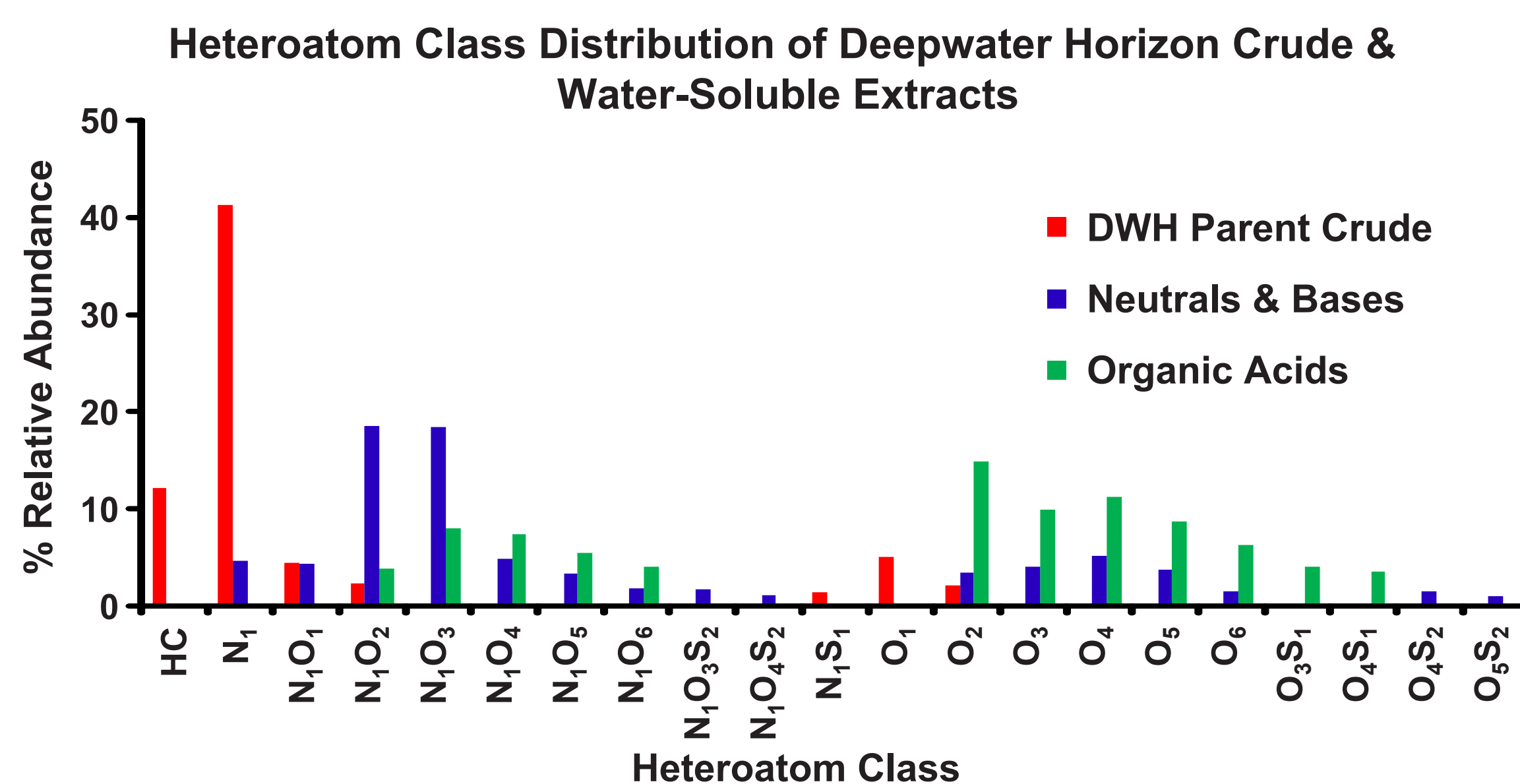


Figure 2. Heteroatom class distribution (for classes >1% relative abundance) of the parent DWH crude (red) and its water-soluble extracts, neutrals & bases (blue) and organic acids (green) by (-) ESI FT-ICR MS. The parent crude oil is less complex in class composition (HC, N₁, N₁O₁, N₁S₁, O₁ and O₁) whereas the water-soluble extracts have an increase in complexity as they contain species that are more oxygenated (N₁O₁, N₁O₂, N₁O₃, N₁O₄, N₁O₅, N₁O₆, O₂, O₃, O₄, O₅ and O₆) in addition to S_xO_y species.

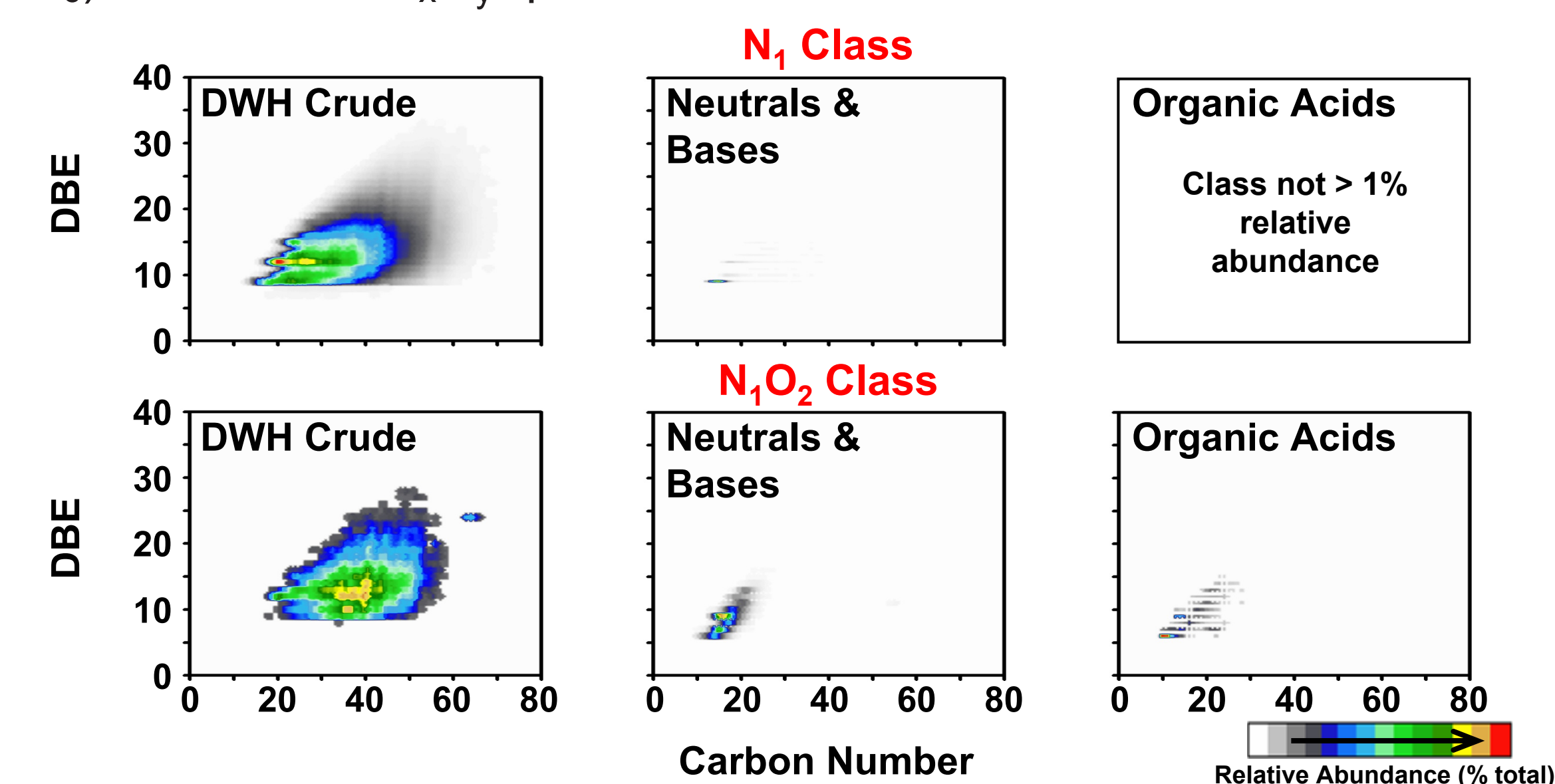


Figure 3. (-) ESI isoabundance color contour plots of double bond equivalents (DBE = number of rings plus double bonds to carbon) versus number of carbons for N₁ (top) and N₁O₂ (bottom) classes in the DWH crude (left), neutrals & bases (middle) and organic acids (right).

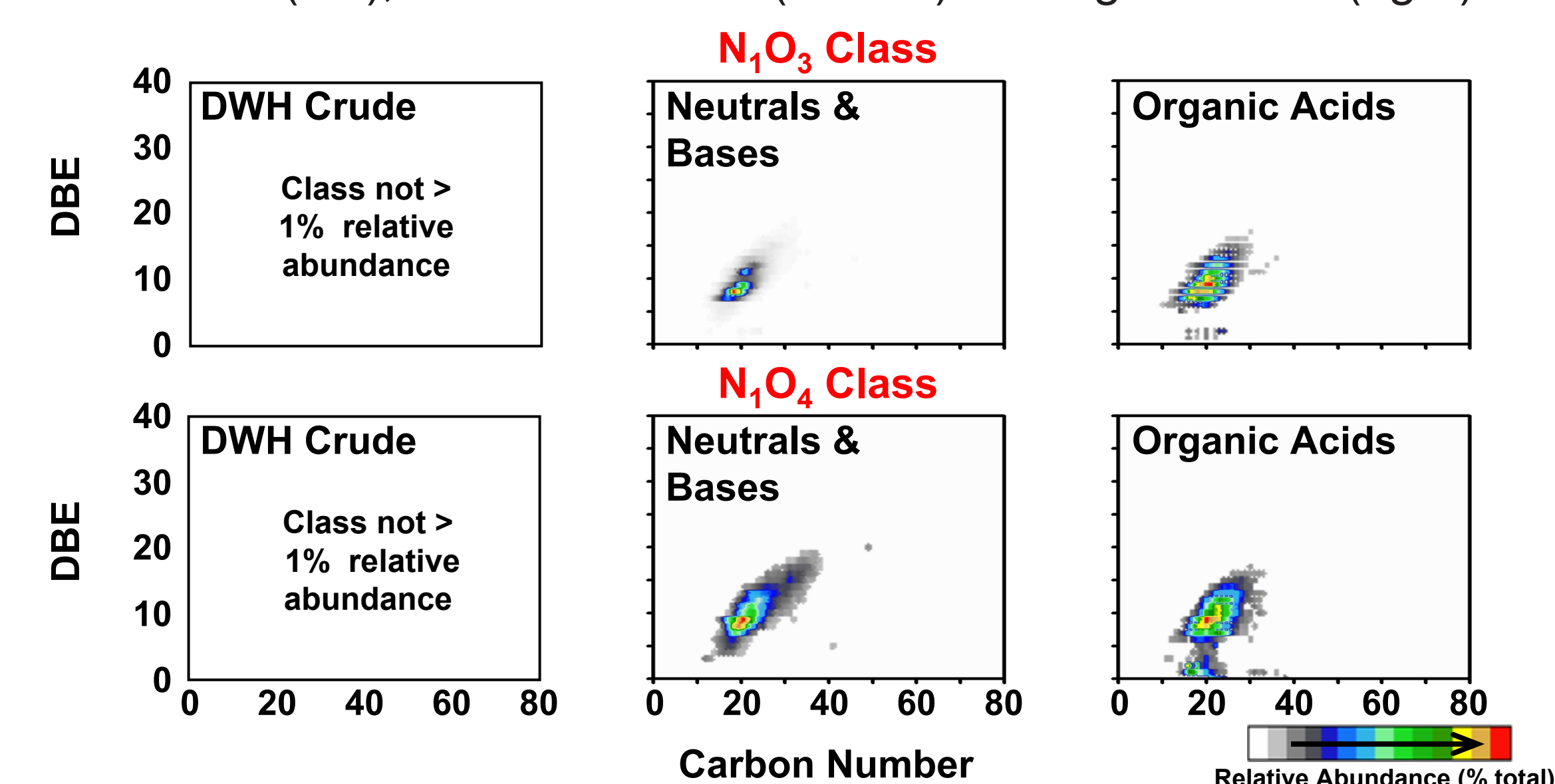


Figure 4. (-) ESI isoabundance color contour images for N₁O₃ (top) and N₁O₄ (bottom) classes in the DWH crude (left), neutrals & bases (middle) and organic acids (right).

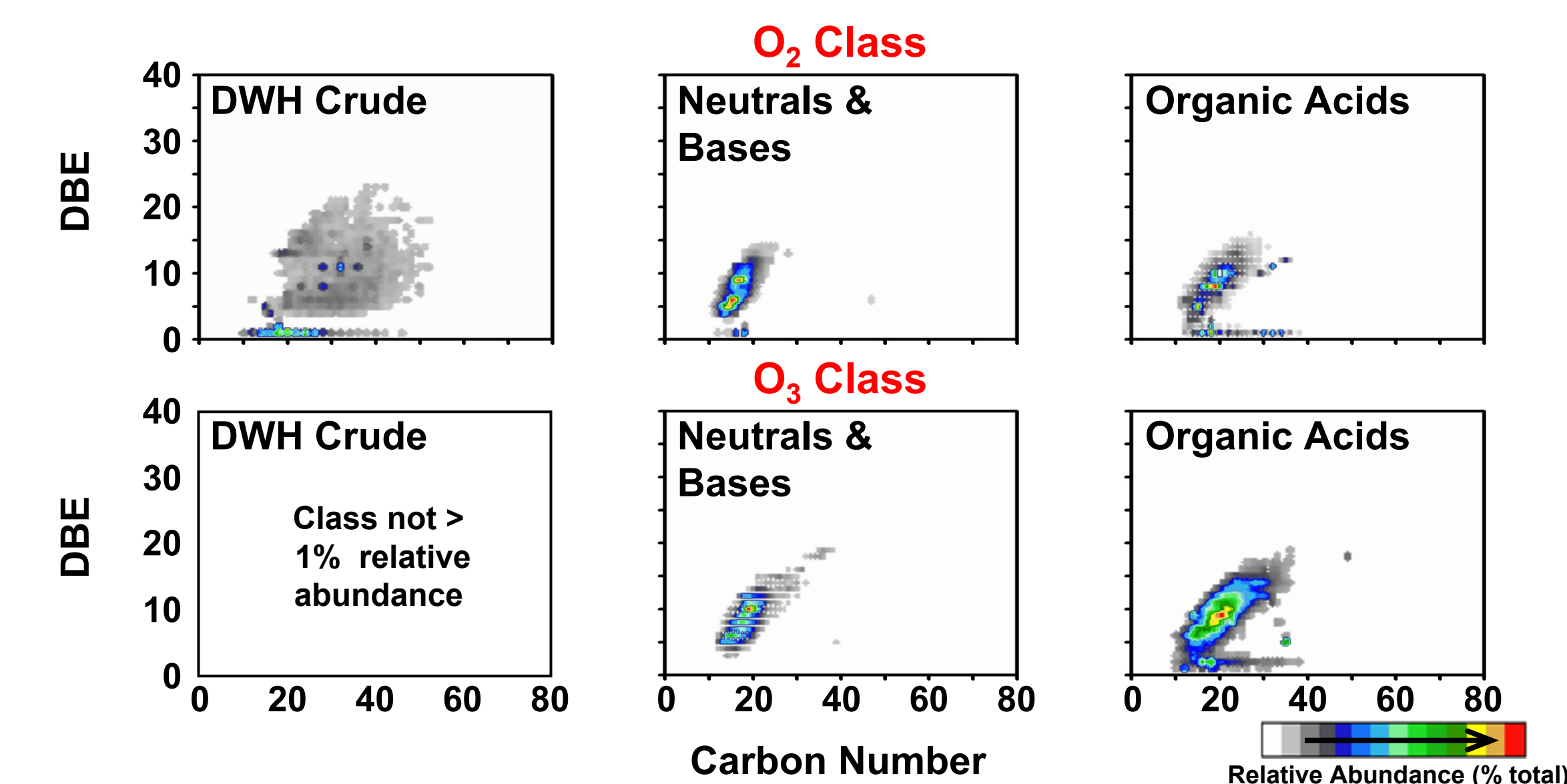


Figure 5. (-) ESI isoabundance color contour images for O₂ (top) and O₃ (bottom) classes in the DWH crude (left), neutrals & bases (middle) and organic acids (right).

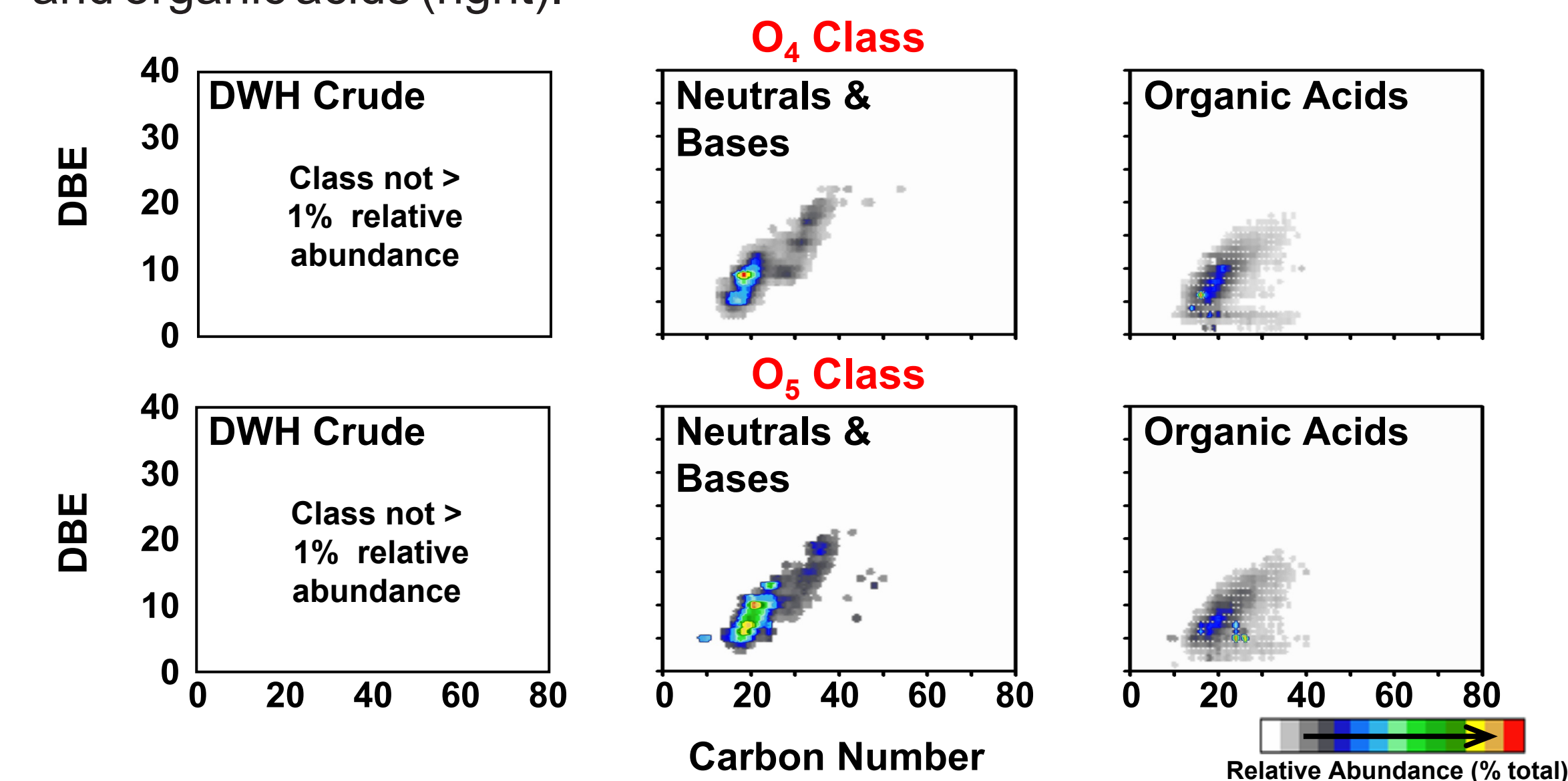


Figure 6. (-) ESI isoabundance color contour images for O₄ (top) and O₅ (bottom) classes in the DWH crude (left), neutrals & bases (middle) and organic acids (right).

Conclusions

Compared to the DWH crude, there is a prevalence of higher oxygen-containing compounds in both water-soluble extracts. Within each water-soluble heteroatom class, there is a reduction in complexity evident by loss of compounds with carbon numbers > 40 relative to the parent crude (C# up to 75) as well as a shift in compositional space to lower carbon number and aromaticity. Previous results have shown a link between compounds with lower carbon number and aromaticity and increased water solubility.^{1,3}

Acknowledgments

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References

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