

Characterization of Sulfur Components in Field Samples from Historic Oil Spills and Seeps

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INTRODUCTION

Nine years after the Deepwater Horizon (DWH) oil spill in the Gulf of Mexico and two decades after the Exxon Valdez spill off the coast of Alaska, both still haunt the future of the oceanic ecosystem. Although the environmental ecosystem of these two oil spills differ, oil-degrading microorganisms play an essential role in both.¹ In studying these two historic oil samples, we also compared them to the natural seep of Carpinteria located in California. Natural seeps or tar pits are natural asphalt lakes, for example the Carpinteria seep in Santa Barbara, California. The Carpinteria seep is located directly on the beach and generates from the underlying California offshore oil field. Natural seeps occur when liquid and gaseous hydrocarbons escape the Earth's atmosphere and surface with low pressure.

Comparison of a natural oil seep (Carpinteria) to field samples from a light crude oil spill (Macondo well oil from DWH) and a heavy crude oil spill (Exxon Valdez), requires Soxhlet extraction prior to analysis. Following Soxhlet extraction, the samples were subjected to a previously published separation which fractionates oil samples based on their sulfur reactivity into three fractions: non-reactive sulfur, reactive sulfur, and mercaptans. Fractions were then characterized by ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to provide molecular-level information about each sample. Through these techniques, the impact of sulfur content on transformation products in the environment can be investigated.

METHODS

Sample	Original Mass (g)	Extracted Mass (mg)	% Yield
Carpinteria	7.95g	914.8mg	11.5%
Deepwater Horizon	4.47g	552.3mg	12.4%
Exxon Valdez	2.92g 1 st extract 1.6714g 2 nd extract	28.9mg 1 st extract 36.8mg 2 nd extract	0.989% 1 st extract 2.2% 2 nd extract

Table 1. Original mass, extracted mass, and total yield for each Oil sediment in Soxhlet Extraction

Three field samples were collected from different sites following large oil spills and subjected to Soxhlet extraction prior to molecular-level characterization by FT-ICR MS. Two of these samples are from the largest oil spills in history: Exxon Valdez (1992) and DWH (2010). These samples are compared to the natural Carpinteria seep. Previous studies have shown that in order to understand the effect these oil spills have on the ecosystem, further experiments that closely look at characterization and molecular data are significant for ongoing research.

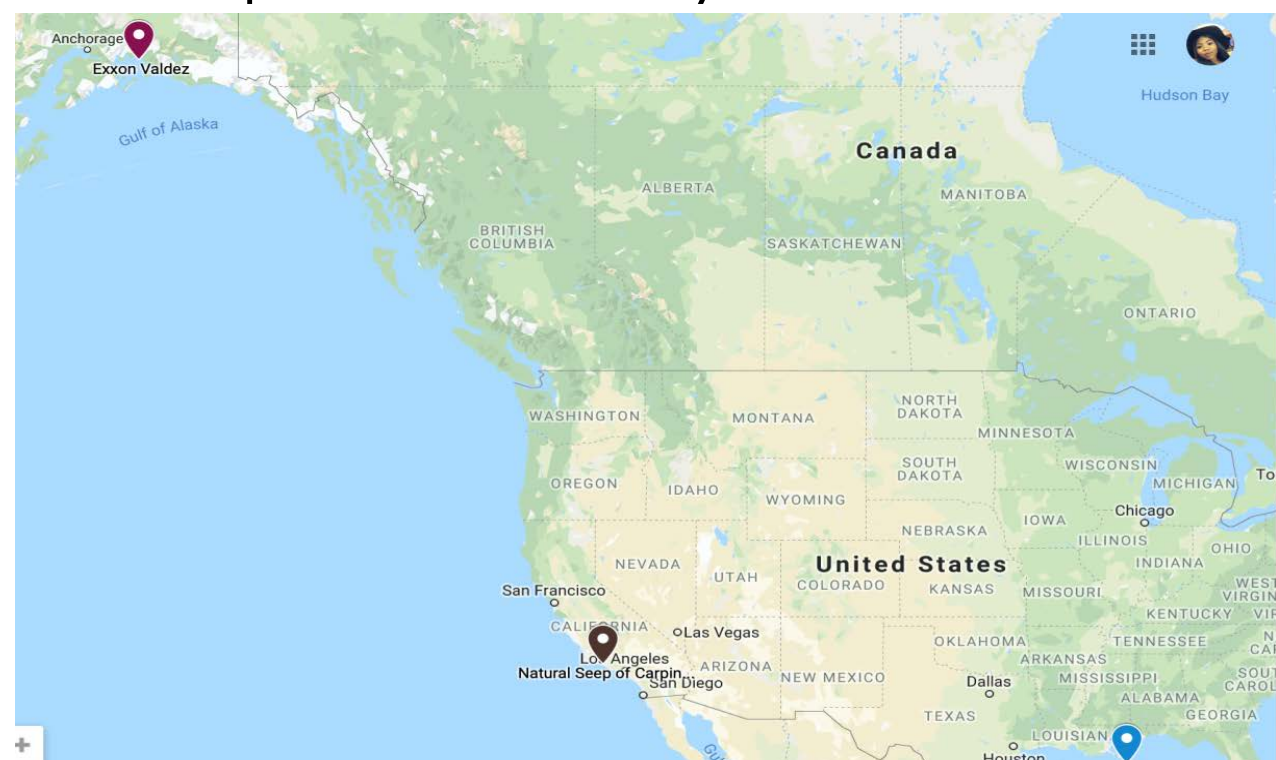
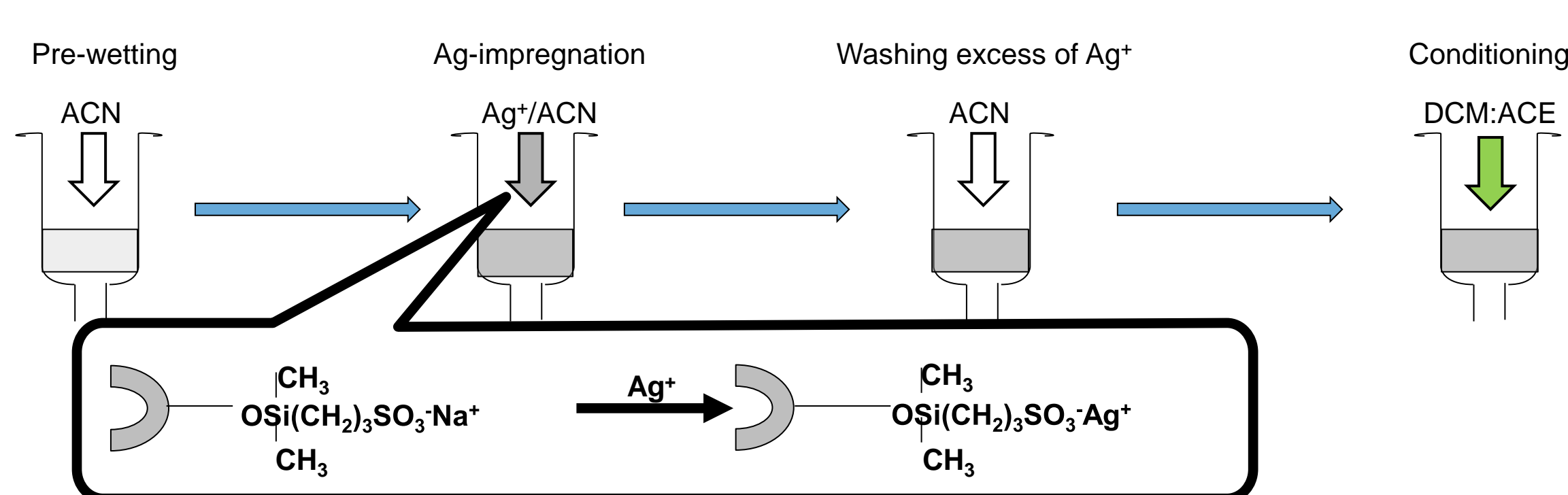


Figure 1: Sampling Locations

Field samples were collected at the point in the top left corner (Exxon Valdez) and bottom right corner (DWH) following oil spills. Exxon Valdez (1992) and DWH (E, 8 May 2017 O3). The bottom left image is a representation of the natural seep of Carpinteria. The percentage of water in these samples varies based on different outgoing tides and incoming tides from their respective sites.

Following collection of field samples, organic compounds were Soxhlet extracted using DCM (dichloromethane) as the solvent.² Each sample performed the extraction in 90:10 DCM; MeOH for 12-24 hours (or until the next day) to remove oil-soluble compounds and were dried under N₂ in a pre-weighed vial. Each vial was then weighed to determine the amount of extracted mass. Table 1 shows the original mass, total mass extracted, and the percent yield for each of the oil sediments.

Stationary Phase Modification



Separation with Ag-impregnated Sorbent

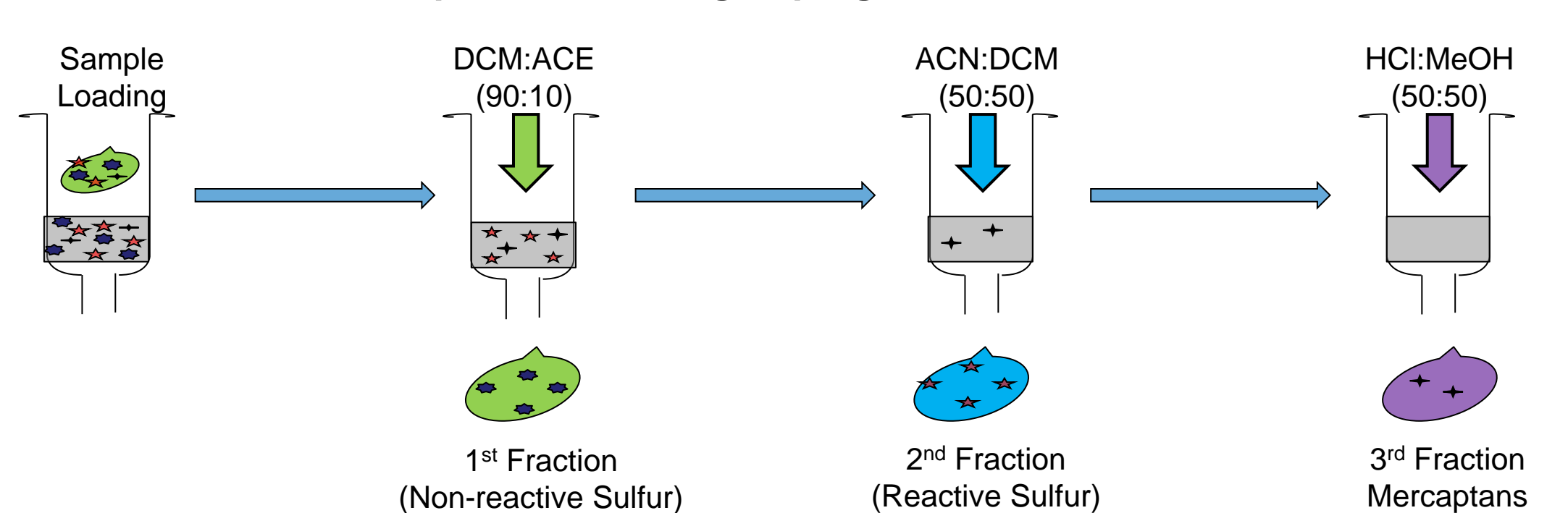


Figure 2: Schematic of sulfur separation. Oil-soluble field samples were extracted via Soxhlet before being loading into SPE cartridges. (Top) The top panel outlines stationary phase in cartridges when conditioned with ACN, AgNO₃ solution and rinsed with ACN to remove any unbound Ag⁺. This process allows the modification of Ag⁺ so that the capacity of Ag⁺ is equal to the first ion exchange of the stationary phase. (Bottom) The bottom panel outlines the procedure for conducting the separation of different sulfur-containing species from petroleum samples.

High sulfur content in crude oil can affect production and refinery operations in the petroleum industry, and can post a threat to human health and the environment following a spill, as many sulfur-containing functionalities have high toxicity.³ In order to understand how the sulfur content affects the transformation products formed after a spill, field samples are subjected to the sulfur separation prior to MS analysis. Through the separation, we can investigate which oils (high or low S-content) produced reactive and non-reactive sulfur in the environment following a spill. Following SPE extraction, each fraction was dried under nitrogen, and subjected to positive-ion (+) and negative-ion (-) electrospray ionization (ESI) 21 Tesla FT-ICR MS.

Sample	Percentage Sulfur	Weight Classification
Deepwater Horizon	0.39%	Light Crude
Exxon Valdez	1.11%	Heavy Crude
Carpinteria 3.7	3.00%	Heavy Crude

Table 2: Sulfur content in each whole crude oil studied after release into the environment. The virgin crude oils range in sulfur content (from 0.39% to 3.00%)⁴⁻⁶, and thus will likely produce different transformation products through weathering processes in the environment.

DISCUSSION

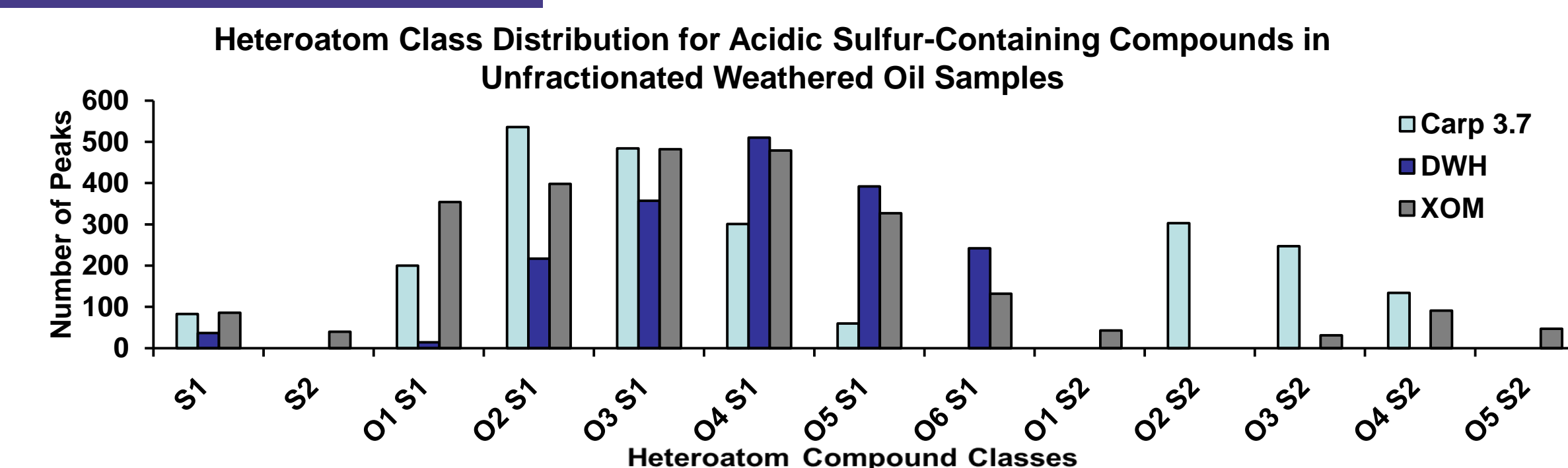


Figure 3: Heteroatom compound class distribution derived from negative-ion electrospray ionization FT-ICR MS at 21 Tesla for sulfur-containing compounds detected in whole field samples. All samples contain S₁ and O_xS₁ compounds, however only Carpinteria and Exxon Valdez field samples yielded appreciable amounts of O_xS₂.

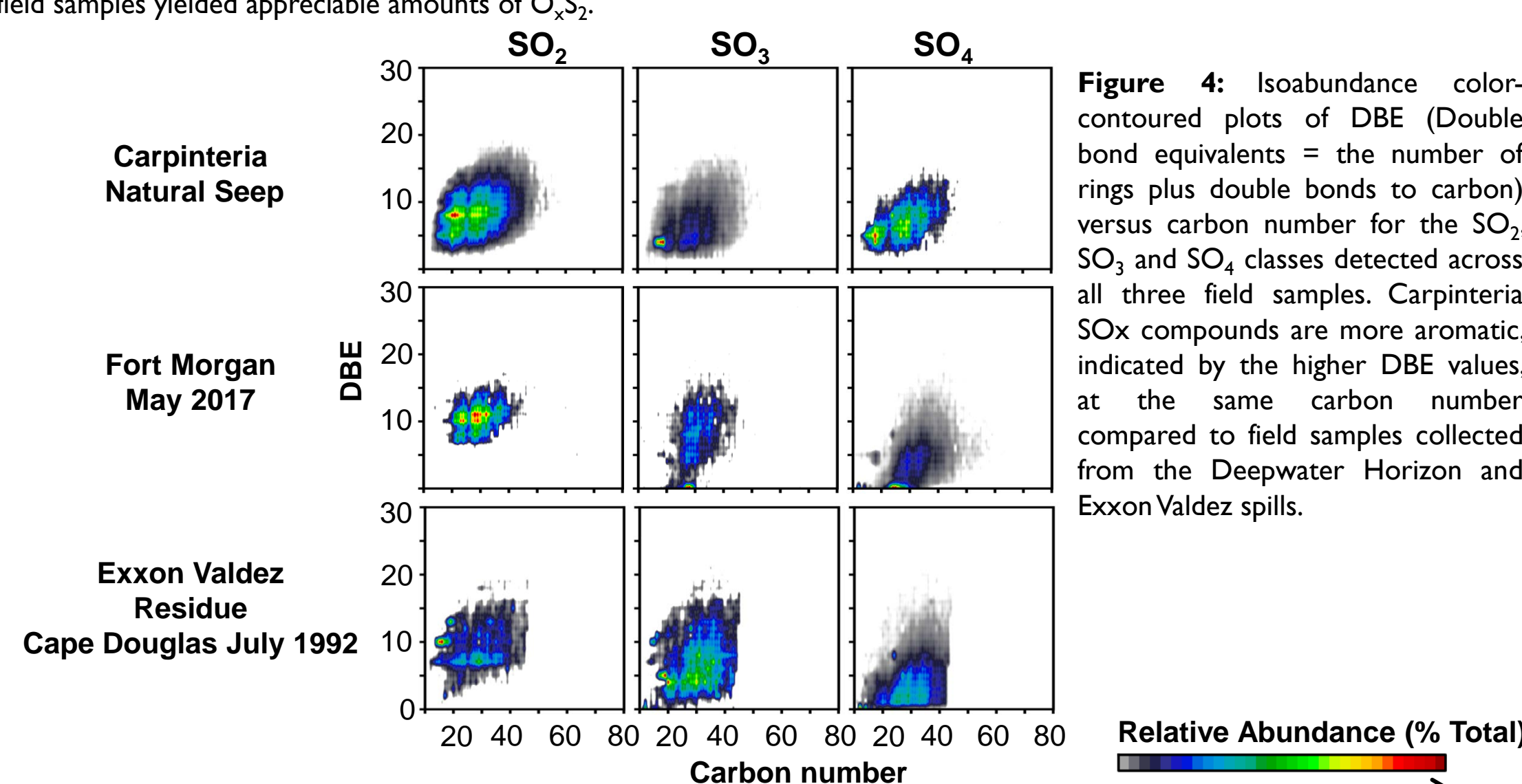


Figure 4: Isoabundance color-contoured plots of DBE (Double bond equivalents = the number of rings plus double bonds to carbon) versus carbon number for the SO₂, SO₃ and SO₄ classes detected across all three field samples. Carpinteria SO_x compounds are more aromatic, indicated by the higher DBE values, at the same carbon number compared to field samples collected from the Deepwater Horizon and Exxon Valdez spills.

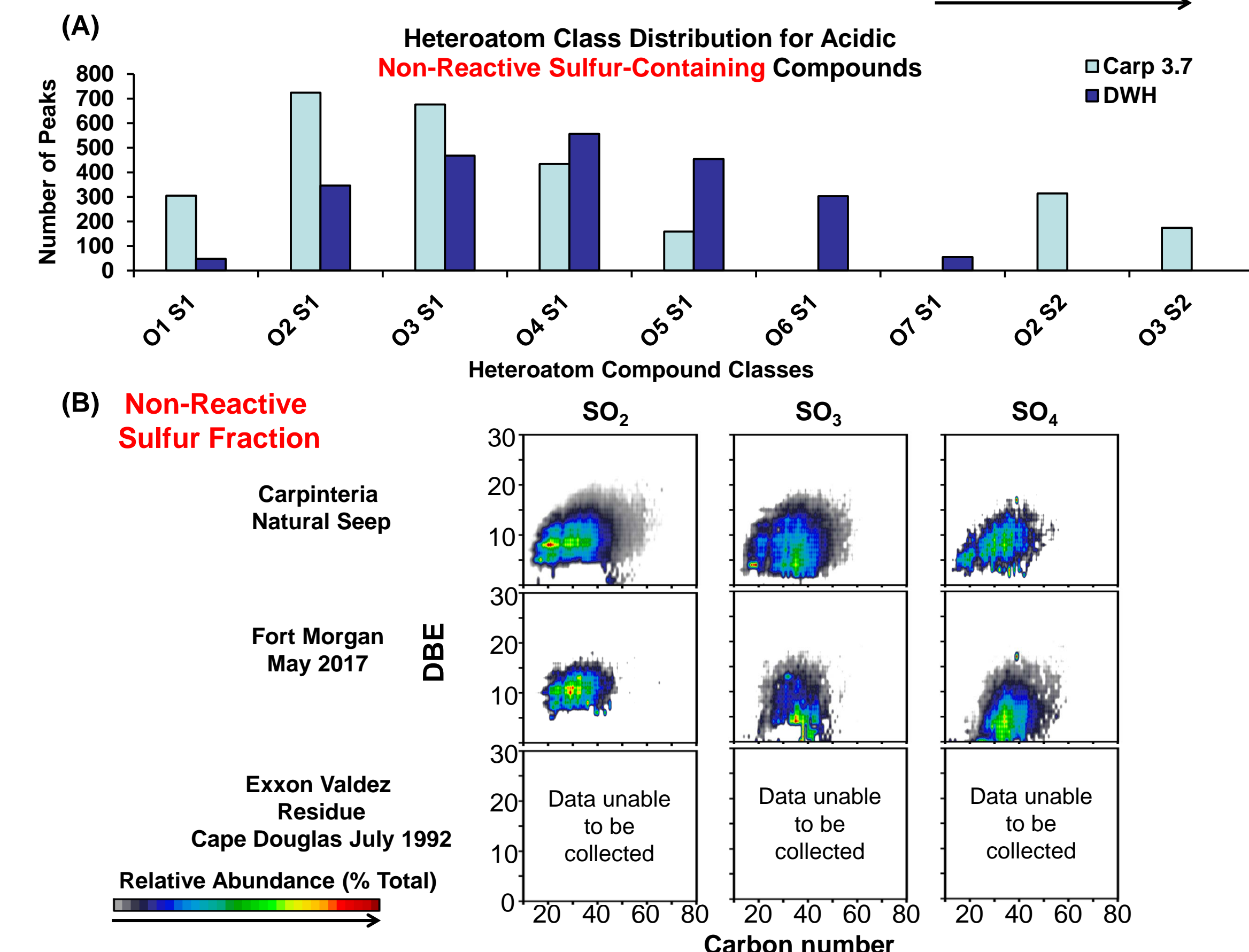


Figure 5: Non-reactive acidic heteroatom class distribution (A) derived from negative-ion ESI FT-ICR MS at 21 T (top) and (B) Isoabundance color-contoured plots of versus carbon number for the SO₂, SO₃ and SO₄ classes detected in non-reactive sulfur fractions from Carpinteria natural seep and Fort Morgan May 2017. The Exxon Valdez sample was too highly contaminated with non-oil compounds to be processed.

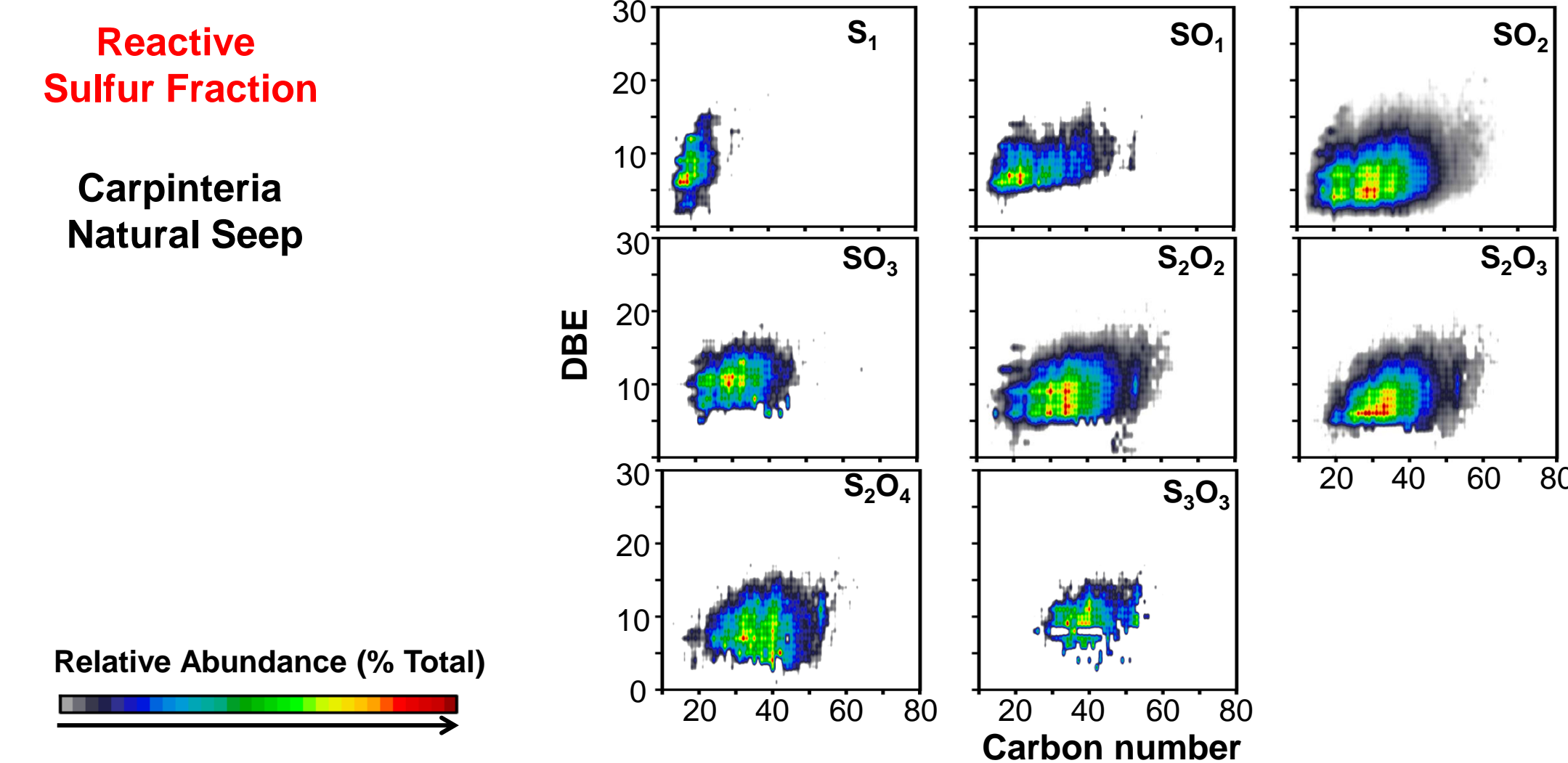


Figure 6: Reactive acidic heteroatom class distribution for reactive acidic classes detected in Carpinteria terrestrial seep sample. Only Carpinteria was able to be collected in time for this presentation.

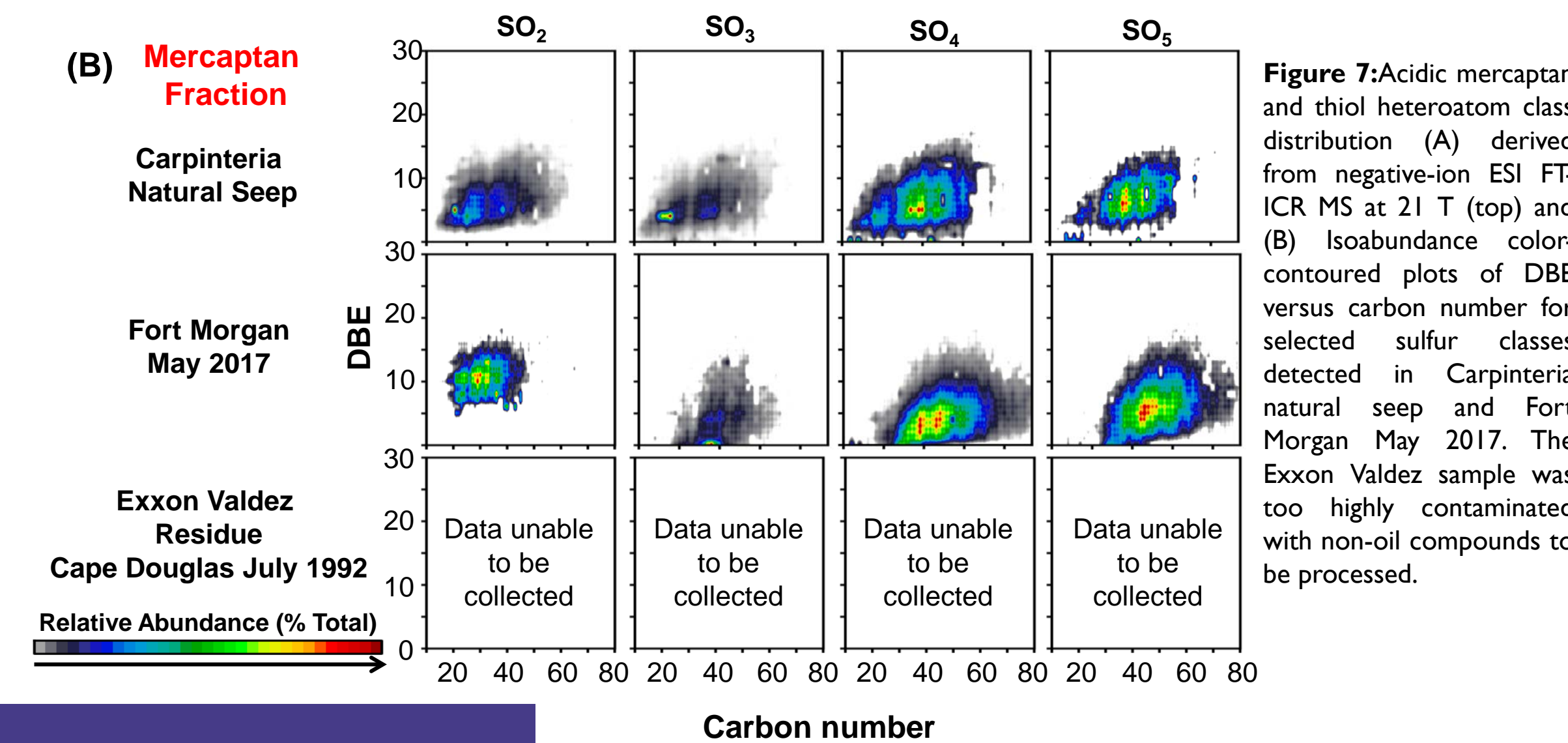
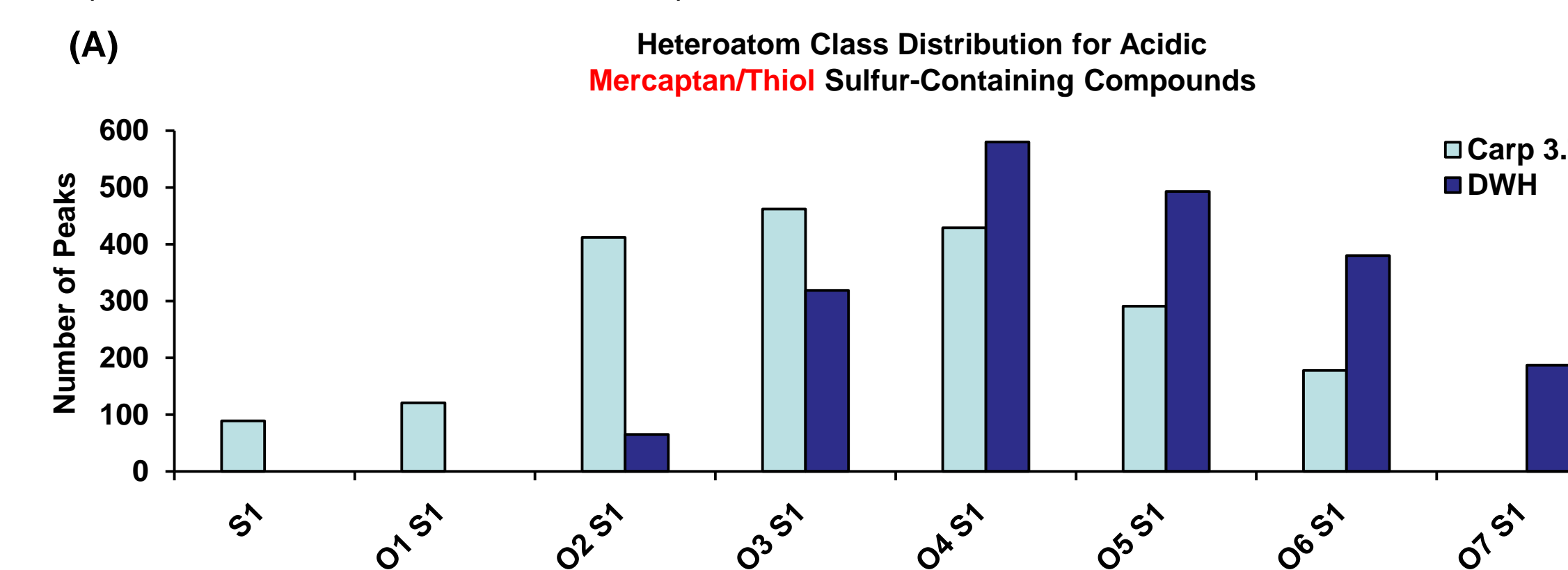


Figure 7: Acidic mercaptan and thiol heteroatom class distribution (A) derived from negative-ion ESI FT-ICR MS at 21 T (top) and (B) Isoabundance color-contoured plots of DBE versus carbon number for selected sulfur classes detected in Carpinteria natural seep and Fort Morgan May 2017. The Exxon Valdez sample was too highly contaminated with non-oil compounds to be processed.

CONCLUSIONS

- Unfractionated Carpinteria and DWH field samples contained high amounts of sulfur-containing transformation products, compared to the Exxon Valdez samples, despite Exxon Valdez virgin crude oil's high sulfur content.
- All three samples contained high amounts of O_xS₁ classes, and Carpinteria and Exxon Valdez samples were enriched in O_xS₂ compounds
- Carpinteria exhibited a distribution of S_xO_y and S_x reactive and non-reactive sulfur compounds, whereas the other two did not contain appreciable amounts of reactive/non-reactive sulfur.
- Carpinteria and DWH field samples contained high amounts of S₁O_x mercaptan/thiol compounds, whereas the Exxon Valdez samples did not.

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Acknowledgements

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