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The Stochastic Nature of Carboxyl Groups in Dissolved Organic Matter across the World's Oceans

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Dissolved organic matter (DOM) is one of the most complex mixtures known, with only 5% of marine DOM characterized at the molecular level. Ultrahigh-resolution mass spectrometry is the primary technique for molecularly analyzing DOM, but when not applied in combination with other analytical methods, it typically provides limited structural information. To enhance structural analysis, chemical derivatization offers a strategy to selectively target functional groups. In this study, we converted carboxyl groups of DOM isolated from three different water masses (fluvial as well as surface, and deep Pacific Ocean) to their corresponding methyl esters using isotopically labeled diazomethane. The reaction products were characterized using Fourier-transform ion cyclotron resonance mass spectrometry. To account for the significant increase in the number of detected masses – more than quadrupling due to derivatization – spectra were acquired in absorption mode.

The conversion of reacted compounds closely followed a log-normal distribution. In accordance with the central limit theorem, this suggests a stochastic reactivity of carboxyl groups across all DOM compounds. The only exception was observed for fluvial DOM, which exhibited a bimodal pattern, indicating the presence of two distinct compound groups with specific reactivity characteristics. Additionally, carboxyl groups were stochastically distributed across the molecular space, with their abundances influenced primarily by the elemental composition of the respective molecular formula and the water type (Figure 1). Computational isomer enumerations supported this stochastic distribution.

We developed a model based on the stochastic distribution of carboxyl groups in DOM to assess their relative abundances across more than 1,000 samples from major oceanic water masses on the globe. A mass spectrometry-derived molecular degradation index correlated positively with the mean number of carboxyl groups per molecular formula, consistent with the introduction of carboxyl groups during the oxidation and degradation of organic matter

This study reveals that the reactivity of carboxyl groups in DOM is governed by a stochastic distribution of this functional group, which is directly linked to elemental composition. These findings challenge traditional views of apparent DOM reactivity classes and rather indicate the presence of a reactivity continuum.

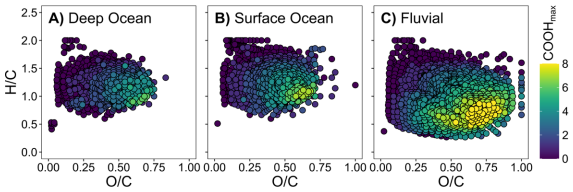

Figure 1: Van Krevelen diagrams of A) deep Pacific Ocean, B) surface Pacific Ocean and C) fluvial DOM, colored by the maximum number of carboxyl groups ($COOH_{max}$) detected for the corresponding molecular formula.