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Universal molecular features of refractory dissolved organic matter in fresh- and seawater

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Dissolved organic matter (DOM) is among the largest pools of reduced carbon on Earth's surface. Its molecular structure and the reasons behind its stability in the aquatic environment are unknown. We present a mathematical model that predicts essential molecular features of refractory dissolved organic matter in fresh- and seawater. The model has only eight input variables and can accurately reproduce the presence and abundance of up to 10,000 molecular formulae in aquatic systems. The model was established with ultrahigh-resolution mass spectrometry data of North Pacific deep water (obtained on a 15 Tesla Fourier-transform ion cyclotron resonance mass spectrometer, FT-ICR-MS).

We determined the molecular formulae of DOM with help of FT-ICR-MS in >1,000 samples from around the globe, covering a wide variety of open ocean, freshwater and coastal systems. The molecular formulae predicted from our North Pacific deep water model were present in all sea- and fresh water samples. In terrigenous DOM, we detected a second group of compounds that could also accurately be predicted with our model, by using a different set of eight input variables. This exclusively terrigenous compound group was more photo-reactive than the universal compound group. During a two-year sampling period at a continental shelf station, the universal DOM compounds were always present at their predicted abundance. During plankton blooms, additional compounds were produced that did not match our model and that did not persist on a longer term. The universal DOM pattern was also not observed in mesocosm experiments where algae and bacteria blooms were artificially induced.

Refractory DOM in any aquatic system not only shares the same molecular formulae at the same relative abundance, but compounds with the same molecular formulae most likely have the same molecular structure, independent of the origin of DOM. Fragmentation experiments in the FT-ICR-MS on a wide range of molecular formulae revealed identical fragmentation pattern in DOM from marine and freshwater systems. We conclude that refractory DOM from any aquatic system has probably the same molecular composition. Even though the number of different compounds in DOM is high, the individual compounds all share common structural features that adhere simple mathematical rules.