



Polycarboxylates as transition state of organic matter in soil, aquatic and atmospheric environment - Evidence from ultrahigh resolution mass spectrometry

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Ultrahigh resolution mass spectrometry as provided by Fourier-transform ion cyclotron resonance mass spectrometry (FTICR-MS) has provided access to the molecular level analysis of complex isolates of natural organic matter. We have analyzed fulvic acids and NOM isolates from surface waters and groundwaters [1], from the deep ocean [2] and from atmospheric aerosol [3] and obtained molecular formulas for several hundred up to several thousand molecules in these isolates. Moreover we have used size-exclusion chromatography-FTICR-MS to compare the molecular formula composition of ions in different size fractions of NOM [4]. These analyses have shown that a common pool of molecular formulas formed from carbon, oxygen and hydrogen appears to be omnipresent in these compartments. The major difference between isolates of different origin is the relative frequency of different molecular species: the more oxygenated or the more unsaturated species may be more frequent in one isolate as compared to another. However, the elemental composition is only one characteristic property of a molecule. Coupled mass spectrometry, such as quadrupole/time-of-flight-MS is indispensable to obtain the complementary structure information [1]. As for the elemental composition a high degree of regularity was also found at the structural level. We concluded that fulvic acids mark a certain state of transition of natural organic matter during its oxidative transformation [1]. These transformation processes removed most of the specific functional groups of the source material, leaving behind chemically less diverse and less reactive polycarboxylates in all environments yet in-

investigated. The regularity in the elemental composition of these molecules, which can also be visualized in specific diagrams, is largely dictated by the rules of stoichiometry. It is still unclear to which extent the differences in the frequency distribution encountered in different samples reflect differences of the source material or are due to diagenetic processes. A larger molecular diversity may be visible in those molecules containing also nitrogen [2, 3]. Here, clear differences in elemental composition and structure have been detected between marine and atmospheric samples, suggesting that the signature of the source material has been preserved or that very specific (trans-) formation processes were effective. FTICR-MS is a new and highly potent tool that will contribute a lot to our understanding of NOM formation, transformation and reactivity at the molecular level in soil and other environmental compartments.

[1] Reemtsma et al. (2006) *Environ. Sci. Technol.* 40, 5839-5845.; [2] Reemtsma et al. (2008) *Environ. Sci. Technol.* 42, in press; [3] Reemtsma et al. (2006) *Anal. Chem.* 78, 8299-8304; [4] Reemtsma et al. (2008) *Water Res.* 42, 63-72.