

DECIPHERING THE RELATIVE INFLUENCE OF PETROGENIC AND BIOGENIC ORGANIC CARBON SOURCES OF A TRANS-HIMALAYAN RIVER USING FT-ICR-MS

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The erosion of terrestrial organic material from active mountain ranges transfers large amounts of particulate organic matter (POM) into long-term geological sinks, such as ocean basins. Rivers are the main agents of this transport. They harvest organic carbon from different parts of their catchments and transport it downstream. Whether the result is a net drawdown or net loss of organic carbon to the atmosphere depends on the type of the eroded carbon and the efficiency of the transport downstream. Transfer of modern or biogenic organic carbon from soils into long-term sinks results in net carbon burial and as such removal of carbon from the short-term cycle. In contrast, a quantitative transfer of fossil, or petrogenic carbon into long term sinks does not affect the carbon budget, but a possible oxidation of petrogenic carbon from sedimentary deposits could result in a net loss of carbon to the atmosphere. It is therefore crucial to establish reliable tools to distinguish between different types of POM and to understand its sourcing and transfer in detail.

Bulk stable and more recently radiogenic isotope values of the organic matter ($\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$ and $\Delta^{14}\text{C}_{\text{org}}$) have routinely been used to unmix different carbon sources of POM exported by rivers. These studies show that the amounts of petrogenic and biogenic organic carbon exported into the oceans are generally controlled by physical erosion but also influenced by other factors such as precipitation and seismicity (e. g. Galy et al. 2015; Hilton et al. 2008; Hilton et al. 2012). Radiocarbon data of suspended river sediment also show that pre-aged biospheric carbon is exported by fluvial systems along with fossil (radiocarbon “dead”) and modern material. This influences the relationship between age and type of organic matter (Galy & Eglinton 2011; Marwick et al. 2015) and therefore complicates quantitative assessments and unmixing of these components.

Here we test a new approach to assess the type of carbon exported through river systems using ultrahigh resolution mass spectrometry. Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) allows the simultaneous measurement of a large range of compounds after a relatively straightforward sample preparation. Until now FT-ICR-MS is mainly used in petroleum geochemistry and DOM studies. We test if this method can be used for fingerprinting particulate organic carbon from different sources in the earth surface system and to trace the export and mixing of POM along river systems. FT-ICR-MS measurements on solvent extractable organic matter hold the potential of distinguishing the POM carbon pools, as they provide direct information on the compositional variability of POM. Combining this information with bulk ^{14}C ages should allow for discrimination between a „pre-aged carbon pool“ composed of a mixture of young and old material, or derived from a pre-aged soil only. We employ this method to decipher the different sources of POM and their export along the Kali Gandaki River, a major trans-Himalayan river characterized by abundant petrogenic carbon bearing Jurassic sediments in the upper catchment as well as aged and modern soils and ample standing biomass.

In a first step, we analyzed end-member samples from the upper catchment containing different types of particulate organic matter such as litter, soil and Jurassic shale. The results of electrospray ionization (ESI-) FT-ICR-MS in negative ion mode showed significant differences in the elemental composition of the different samples, confirming the viability and potential of the method. In the shale, we observed abundant condensed hydrocarbons in the O_x classes and N_1 compounds. Soil and litter samples showed abundant O_x compounds from O_2 to O_7 as well as N_1O_5 compounds. With increasing oxygen number the DBE equivalents and carbon numbers increase.

To characterize the routing of organic carbon along the Kali Gandaki we analyzed suspended sediment and flood deposit samples collected at representative river locations during two consecutive monsoon seasons. Bulk data revealed a trend along the river with decreasing $\delta^{13}C_{org}$ values and TOC concentrations from the upper catchment through the mountain range. In the lower catchment, TOC concentrations increased slightly, but the $\delta^{13}C_{org}$ values continued to decrease. Radiocarbon ages of the samples from the upper catchment were between 10 and 20 kyr, suggesting that petrogenic carbon input dominates POM in the upper catchment, especially in shale draining tributaries. In the lower catchment, significantly younger radiocarbon ages were measured (300-10'000 years), suggesting overprinting or replacement of the petrogenic carbon by biospheric POM. The negative ion mode ESI-FT-ICR-MS measurements of the solvent extractable fraction of all river sediments show a dominance of O_2 compounds and minor abundances of other O_x classes as well as the N_1O_5 class. The N_1O_5 compounds in the sediment samples share characteristics with the soil samples and signal a contribution of soil organic carbon. We are currently evaluating positive ion mode ESI-FT-ICR-MS measurements for this sample set expecting a stronger diagnostic power by combining both ionization modes.

Our first results indicate that ESI-FT-ICR-MS measurements on total lipid extracts are generally suited to distinguish POM types according to their compositional variability. We have shown that it is possible to characterize groups of compounds typical for different types of POM. We are currently investigating how the mixing of these different sources is reflected in the compositional variability of river sediment samples. This information obtained by the FT-ICR-MS is complementary to radiocarbon data and potentially capable of detecting compositional changes in POM during transport processes and can therefore help to better constrain and understand POM fluxes in complex environments such as mountain ranges with strong topographic, geomorphic and climatic gradients.

References

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