EVALUATION OF RIVERINE DOC EXTRACTION METHODS FOR RADIOCARBON DATING

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Riverine discharge of dissolved organic carbon (DOC) represents an important part of the global carbon cycle. Substantial effort is invested to characterise the chemical and isotopic composition and to determine flux rates of terrestrial DOC to the oceans to determine potential influence on and response to climate change. Data quality and comparability largely depends on the careful evaluation of methods used to molecularly and isotopically characterise the DOC fraction. For radiocarbon dating, it is required to isolate the DOC from the water medium and to oxidise the organic matter to CO_2. Currently a variety of methods are being used either to isolate DOC followed by combustion (solid phase extraction; roto-evaporation) or to directly oxidise DOC to CO_2 (chemical; photochemical oxidation). Here we report on and compare the extraction efficiency, blank carbon incorporation, data reliability and methodological limitation associated with ultraviolet photochemical oxidation (UVO), roto-evaporation (RV) and solid phase extraction (SPE).

Aqueous solutions of authentic standards (oxalic acid; glycine hydrochloride; 4-hydroxybenzaldehyde and *p*-coumaric acid) with known radiocarbon composition were processed in duplicates alongside a natural DOC sample (collected from the "Kuhgraben" at the University Bremen). UVO (performed on a custom build UV photochemical oxidation system at NOSAMS, WHOI, USA) showed elevated blank carbon incorporation (8.2 ± 5.3 µg) and very high extraction efficiency for natural samples (oxidation of ~100 % DOC to CO_2). RV showed the smallest blank carbon incorporation (1.9 ± 1.2 µg), but lower extraction efficiency (~ 70 %). SPE using a styrene-divinylbenzene polymer (PPL) cartridge showed highest blank carbon incorporation (10.4 ± 6.7 µg) and lower extraction efficiency (~ 70 %), however the non-polar polymer could not retain the short chain, polar glycine hydrochloride and oxalic acid standards.

UVO possibly provides the most reliable radiocarbon ages for riverine DOC, as near complete oxidation is achieved and blank carbon incorporation is small. However, it requires an expensive and custom build UVO system, which might be unavailable to the broader community. RV provides an inexpensive and reliable alternative, although the elevated temperatures potentially discriminate against highly volatile, low molecular weight fraction of DOC. SPE incorporates high amounts of blank carbon, possibly from partial dissolution of the polymer. Additionally, SPE using PPL-cartridges potentially discriminates against the biologically active, short chain and polar constituents of the DOC fraction, and should be used with care for radiocarbon dating.