



Source apportionment of methane using a triple isotope approach – Method development and application in the Baltic Sea

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We present a method for measurements of the stable and radiocarbon isotope systems of methane in seawater and sediments. The triple isotope characterization of methane is useful in distinguishing different sources and for improving our understanding of biogeochemical processes affecting methane in the water column. $\delta^{14}\text{C}-\text{CH}_4$ is an especially powerful addition to stable isotope analyses in distinguishing between thermogenic and biogenic origins of the methane. Such measurements require large sample sizes, due to low natural abundance of the radiocarbon in CH_4 . Our system for sample collection, methane extraction and purification builds on the approach by Kessler and Reeburgh (Limn. & Ocean. Meth., 2005). An in-field system extracts methane from 30 -120 l water or 1-2 l sediment (depending on the in-situ methane concentration) by purging the samples with Helium to transfer the dissolved methane to the headspace and circulating it through cryogenically cooled absorbent traps where methane is collected. The in-field preparation eliminates the risks of storage and transport of large seawater quantities and subsequent leakage of sample gas as well as ongoing microbial processes and chemical reactions that may alter the sample composition. In the subsequent shore-based treatment, a laboratory system is used to purify and combust the collected CH_4 to AMS-amenable CO_2 . Subsamples from the methane traps are analyzed for stable isotopes and compared to stable isotope measurements directly measured from small water samples taken in parallel, to correct for any potential fractionation occurring during this process.

The system has been successfully tested and used on several shorter shipboard expeditions in the Baltic Sea and on a long summer expedition across the Arctic Ocean. Here we present the details of the method and testing, as well as first triple isotope field data from two cruises to the Landsort Deep area in the Central Baltic Sea.