# Tritium/$^3$He dating of ocean waters: Early and recent applications

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Soon after the discovery of $^3$He in the ocean at the end of the 1960's it was recognized that whereas much of the $^3$He excess in the deep ocean is due to injection of mantle helium into the intermediate waters of the ocean, there is another distinct $^3$He signal in the shallow water column derived from the decay of tritium. This signal offers the possibilty to use the ratio of tritium and $^3$He as a radioactive clock in studies of the age structure and spreading of water masses in the ocean.

Since the early applications of the method by Jenkins and Clarke [1] tritium/$^3$He dating has found many applications in oceanographic studies. We highlight some of the applications of tritium/$^3$He dating to oceanographic problems including spreading of water masses in well defined current systems with emphasis on the Arctic Ocean, deep water formation estimates in the Nordic seas, and variability of deep water formation in the Greenland Sea using tritium/$^3$He time series.

Whereas early studies used the apparent tritium/$^3$He ages in a straightforward manner as a unique ventilation age, later applications applied a variety of methods to correct for non-linearities in tracer ages that are inherent to the tritium/$^3$He method in the presence of mixing. Newer methods combine modeling results with the observed distributions of multiple tracers to yield a more complete picture of tracer age. We briefly discuss such methods for correction of non-linearities in the tritium/$^3$He ages.

[1] Jenkins, W. J. & W. B. Clarke, (1976). The distribution of $^3$He in the western Atlantic Ocean. *Deep-Sea Research*, **23**, 481.

# Quantification of methane emissions from pockmarks (Lake Constance) by online and onsite membrane inlet mass spectrometry

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The importance of mud volcanoes, cold seeps, gas hydrates and pockmarks for emissions of methane is underlined by observations of bubble plumes by underwater camera systems as well as acoustic techniques. Compared to such semi-quantitative information, rather little-known is the concentration field of $CH_4$, a requirement for calculations of budgets, at such sites. This is mainly due to laborious sampling schemes (e.g. by Rosette Water Sampler) or rather time consuming $CH_4$ analysis (e.g. by gas chromatography) during research cruises.

By application of membrane inlet mass spectrometry, applying the Inspectr200-200 [1, 2] which is designed for *in situ* measurements down to water depths of 200m and allows gas analysis with a scan rate of <2 seconds, we investigated the $CH_4$ concentration around pockmarks in Lake Constance. The pockmarks are located in water depths of 13m to 80m.

During the research cruises we applied the Inspectr 200-200 onboard of the vessel and used a submersible pump system for continuous water sampling. By this means we analysed the concentration field of $CH_4$, $O_2$, Ar, as well as $N_2$ for different water depths along transects crossing the pockmarks.

Very steep horizontal and vertical gradients of methane concentrations were observed in bottom as well as surface waters above pockmarks. An increase in $CH_4$ concentrations by a factor of more than 5 were detected within a distance of less than 10 meters.

By compilation of the continuous gas analyses a 3D visualisation of $CH_4$ concentration field above pockmark sites were computed and estimates on gas emissions from the seafloor were derived.

[1] Short *et al.* (2006) *Trends Anal. Chem.* **25**, 637–646. [2] Schlüter (2008) *J Am Soc Mass Spectrom* **19**, 1395–1402.