

## ***Interactive comment on “Methane oxidation in permeable sediments at hydrocarbon seeps in the Santa Barbara Channel, California” by T. Treude and W. Ziebis***

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This paper makes a useful contribution to the limited data on shallow gas seeps, although it is a very incomplete story without deeper samples and with the limited number of cores taken, given the variability of the environment. The studies most related to those in the present paper were those carried out on the methane seeps that occur in sandy sediments, from the intertidal to 12 m depth, in the Kattegat (Jensen et al. 1992, Dando et al. 1994b, Schuster 1994). Schuster carried out extensive studies with labelled methane to determine the zones of methane oxidation and current carbonate deposition. It would be useful to include a comparison with the Kattegat studies.

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Interpreting geochemical profiles around gas outlets in coarse sediment in shallow water is difficult, because the gas escape routes are rarely vertical, buried shells and stones disrupt flow patterns (Dando et al. 1994 a) and sand movement due to storms continually disturb the sediment profiles and can bury methane gas pockets. Taking sediment cores is a problem due to sediment disturbance when the core is inserted and the near impossibility of sealing the core base without disturbance of the profiles at the base of the cores. Hammering 5 cm diameter cores into the sand will disrupt the profiles, when compared with those seen using sippers, or diffusion plates that are left in place until equilibrium has been achieved. This was demonstrated by the core at 400 cm that voided gas when the tube was hammered into the sand. With cores, we used to gently push a bung, with an open tap, into the core tap, to minimise applied pressure, and then close the tap to seal. After digging down to the base of the core the core base was capped externally. However, a comparison of similar cores of different lengths showed that at least the bottom 5 cm of each core had a profile modified by the ingress of seawater. In the present study, the cores were very short and many showed a methane peak in the region of 4-6 cm. This may be due to disturbance or to a higher porosity layer at this depth. The porosity data is not shown, to establish if there is a link. With a gravel layer underneath, the highest methane would otherwise be expected at the core base. We are informed that at the Brian site the penetration problem was due to gravel, rather than carbonates, although carbonate deposits are reported at the seep. In the Kattegat there were high aerobic oxidation rates on exposed carbonates and aerobic oxidation activity was found from 0 - 2 cm to 0 -13 cm depth at different sites (depending on current). Oxygen penetrated to 5 cm depth at some sites, probably deeper in the high intertidal. Peak sulphate reduction rates were usually within 10 cm of the surface, and there was not always a second minor peak at depth. Sulphate reduction rates were often high due to organic matter buried after sand movement. The depth of peak anaerobic methane oxidation also varied from core to core but was commonly at 10 - 20 cm depth in seep and near-seep cores. There was a greater variability in the depth of the peak rate of deposition of methane-C as carbonate (probably

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because of varying DIC pool sizes). These depths were between 10 and 25 cm in seep and near-seep cores. In general, the anaerobic methane oxidation maximum occurred in a zone containing carbonate-cemented sand. Total methane oxidation, integrated over 0-20 cm sediment depth, was above background within 30 cm of a gas outlet, with values up to 15 mmol m<sup>2</sup> d<sup>-1</sup>.

Given the lower oxygen penetration at the Brian site, a peak in anaerobic methane oxidation within the upper 15 cm of sediment would be expected. Peaks in methane oxidation usually coincided with peaks in methane concentration in the cores examined. The authors should be aware that most of the methane in the sand is in the form of free gas, rather than dissolved in the pore water. This could have been seen if the pore water samples were analyzed for methane. The assumption appears to have been made that it was all dissolved in the pore water. A consequence of this is that methane is not evenly distributed across the core at any one horizon, or within the samples used for methane oxidation measurements. The uncertainty about the geochemical profiles and the lack of ANME counts below about 8 cm, means that it is not correct to state in the abstract that "biogeochemical data suggests that the majority of methane is consumed by anaerobic oxidation of methane (AOM) coupled to sulfate reduction below the surface layer (>15 cm)". This may be correct but it is based on the assumption that the rates of MOX at the Brian seep are actually considerably higher than those measured. The authors should consider the implications of the gravel layer for carrying oxygen-containing water underneath the reducing sand. Such a situation is known from much deeper sites. It would depend on where the gravel outcrops and the tidal currents and storm surges.

Another statement in the abstract that is doubtful regards the "known deep-sea seep habitats, where upward fluid advection through more fine-grained sediments leads to an accumulation of AOM activity within the top 10 cm of the sediments". This activity can also be very much deeper at such sites. Studies at methane seeps at approximately 330 m depth in the Skaggerak (Dando et al. 1994b, Dando et al. 2008) found

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this maximum to be 18 cm in one actively bubbling core and 40 cm in another seep core, all in very fine-grained sediment. In near seep samples the active zone could be as deep as 175 cm. Seeps are extremely variable environments and it is very seldom that two similar cores are collected.

Geochemical profiles around seep outlets are not uniform, since a buried shell or stone will disrupt the convective flow and neighbouring gas vents can have an influence. Thus, cores taken at the same distance from a gas outlet can show very different profiles. For this reason alone, using Surfer to 'join' profiles along a transect (fig. 2) makes no sense and the profiles of the individual cores should be shown.

Note that sodium hydroxide strips adsorbed methane from inorganic surfaces so the methane measured is total sediment methane (dissolved + free gas + adsorbed), not just pore water methane and gaseous methane. This will also confuse the isotope ratio data since the adsorbed methane commonly has a very different ratio to the free methane.

The suggested vibrocoreing is not ideal for good geochemical profiles and I would suggest using some form of diffusion devices that are left in the sediment to attain equilibrium before sampling. The paper can be improved by giving details of exactly how the cores were removed, i.e. the steps taken to reduce disturbance of the profiles, and by revising the diagrams so that they are clear when printed on an A4 page. At present, some have to be expanded 4-fold in order to read some of the details. The discussion would greatly benefit from revision with respect to the comments above.

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