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Interactive comment on "Carbon Dioxide and Methane Emissions from Red Sea Mangrove Sediments" *by* Mallory A. Sea et al.

Anonymous Referee #1

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Sea et al. report data on CO2 and CH4 fluxes from a series of mangrove sediments along the Saudi Arabian coast, as well as data on d13C of CO2 and CH4 from their incubation experiments. While the topic is certainly of interest given the relative scarcity of GHG flux measurements from mangrove sediments in arid zones, unfortunately I disagree with the methodology and experimental appraoch, which in my opinion renders the CO2 and d13C-CO2 data incorrect. As outlined below, the methodology does not account for the inorganic carbon system equilibrium (CO2 produced will rapidly re-equilibrate with bicarbonate and carbonate ions) and for isotope fractionation between the different inorganic C species.

Detailed comments

I focus here only on the methodology aspects since in my opinion the approach does

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not measure CO2 emission rates correctly, and the d13C data are similarly not representative. These concerns invalidate the discussion and conclusions on CO2 fluxes and sources of CO2. The authors used 2 different experimental setups to perform their incubations. In both cases, CO2 fluxes are derived from an increase in the partial pressure of CO2 in the water column overlying the sediment in a sediment core; either by directly measuring pCO2 in the water (described in section 2.3.1) or by measuring pCO2 in the headspace above the water column in a sediment-water-headspace incubation (described in section 2.3.2). Both approaches assume that all CO2 produced in – and released from – the sediment accumulates as CO2 in the overlying water, and equilibrates with CO2 in the headspace (for the 2nd approach), but ignores the fact that dissolved CO2 will rapidly equilibrate with dissolved HCO3- and CO3âĂŤ(see for example Schulz et al. Marine Chemistry 100: 53-65 for a discussion on the kinetics of the inorganic carbon equilibration). What should be determined is the change in the total DIC concentration, rather than only looking at CO2. In addition, anaerobic minerization processes within the sediment (sulphate reduction is likely important) may result in the release of bicarbonate rather than CO2, further necessitating the use of total DIC concentration data. The same problem holds for the d13C data, which was measured on CO2 in the headspace (2nd appraoch). Since there is isotope fractionation in the inorganic C system, with CO2 being substantially depleted in 13C relative to bicarbonate, the changes in d13C in CO2 in the headspace are not directly linked to the CO2 produced in the sediment by respiration, but are transformed during equilibration in the water column overlying the sediment, and there is an additional fractionation step between aquous (dissolved) and gaseous CO2 (in the headspace). Hence, the Keeling plot approach will not provide a reliable way of determining the source of CO2 produced – both the concentration and the d13C data determined in the authors' approach are not relevant; it is the total DIC concentrationa and d13C of the total DIC pool (or rather, DIC + CO2 in headspace) that should have been measured.

The CH4 data do appear valid, since they do not suffer from the issues described above for CO2. In principle however, isotope data on methane in the headspace should also

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be corrected for fractionation between CH4 in the water and gas phase; although this will have a marginal effect on the final data and interpretation.

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