

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 approach, 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 CO₃²⁻ (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 mineralization 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 approach). 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 aqueous (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 concentration 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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