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TITLE: Methane Emissions From the Salt Marshes of Doñana Wetlands: Spatio-Temporal Variability and Controlling Factors

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ABSTRACT:

Coastal wetlands are significant sources of methane to the atmosphere, but emissions in these ecosystems are still poorly quantified, as in situ data are limited. In this study, we present the first assessment of spatio-temporal changes in air-water CH₄ fluxes in the salt marshes of Doñana wetlands (SW Spain), one of the most emblematic protected areas in Europe due to its high biotic diversity and unique importance for aquatic wildfowl. The marshes are flooded by estuarine waters from the adjacent Guadalquivir River by tidal intrusion, which must influence aquatic CH₄ dynamics through changes in salinity and water chemistry that affects sedimentary methanogenesis. During sixteen samplings conducted between March 2016 and March 2018, surface water CH₄ concentrations were measured by using static-head space equilibration gas chromatography in seven sites representing salt marshes located in the land strip close to the estuary. Because of meteorological conditions and tide variations, salinity markedly changed across the salt marshes, although sites located closer to the river mouth could be categorized as polyhaline marshes whereas upstream sites formed a group of mesohaline marshes. The CH₄ saturation range was 252-36,735 % (average 5,170%) and 374-620,007 % (average 31,541%) in polyhaline and mesohaline marshes respectively, suggesting inhibitory effect of sulfate on methanogenesis, although a linear trend between dissolved CH₄ concentration and salinity was not observed. In contrast, water temperature and chlorophyll a were significantly and positively correlated with methane, indicating sedimentary methanogenesis control by temperature and organic matter availability boosted by primary productivity. This does not exclude the possibility that some CH₄ might come from estuarine inputs. Air-water CH₄ fluxes ranged from 2.6 to 720 $\mu\text{mol m}^{-2}\text{d}^{-1}$ (average 104 $\mu\text{mol m}^{-2}\text{d}^{-1}$) in the polyhaline marshes and from 5.6 to 12,715 $\mu\text{mol m}^{-2}\text{d}^{-1}$ (average 637 $\mu\text{mol m}^{-2}\text{d}^{-1}$) in the mesohaline marshes, with the higher emissions being measured during the summer months in all sites. Even though the strongest environmental drivers of dissolved CH₄ accumulation seemed to be temperature and productivity, the spatio-temporal patterns observed suggest that methane dynamics in Doñana salt marshes are controlled by a mosaic of processes rather than by a single environmental force.

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