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The relationship between seagrass (*Posidonia oceanica*) decline and sulfide porewater concentration in carbonate sediments

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Abstract

In this study we test the hypothesized negative relationship between seagrass status and porewater hydrogen sulfide (H_2S) levels, through a comparative analysis within a range of seven *Posidonia oceanica* meadows growing over carbonate sediments in the NW Mediterranean Sea around Mallorca Island. The studied meadows range from meadows growing on sediments with very low sulfide porewater concentrations (4.6 μM) to those growing over higher sulfide conditions (33.5 μM). Organic matter content, sulfate reduction rates and sulfide porewater concentrations in the sediments were determined concurrently with the assessment of demographic plant dynamics (specific mortality and net population growth rates). Sulfide porewater concentration increased with increasing organic matter content in the sediment, while net population growth decreased significantly with low increases of sulfide concentrations. Our results confirm the previously suspected vulnerability of seagrass meadows growing on carbonate sediments to increased sulfide levels. An excess of 10 μmols $H_2S\,L^{-1}$ porewater is identified to already conduce *P. oceanica* meadows to decline, which this study identifies, particularly, as strongly sensitive to sulfides. The results reported here suggest that even moderate increases in organic carbon inputs may lead to enhancement of dissolved sulfides and may be an important factor for seagrass status in these iron-depleted carbonate sediments from the Mediterranean Sea.

Keywords: carbonate sediments; demographic plant dynamics; hydrogen sulfide; seagrass; sulphate reduction rate

Regional index terms: Spain; Western Mediterranean Sea; Mallorca and Cabrera Islands

1. Introduction

Seagrass meadows are among the most productive of all marine ecosystems, contributing about 12% of the net production of organic carbon in the ocean (Duarte and Chiscano, 1999), and are valued for their high biodiversity and habitat services. In recent decades, extensive losses of seagrass habitats have been documented worldwide (Nienhuis, 1992; Hemminga, 1998; Duarte, 2002). Causes of decline have been commonly associated with increased eutrophication and consequent degradation of underwater light environment (Orth and Moore, 1983; Cambridge and McComb, 1984; Larkum and West, 1990; Hemminga, 1998). However, light competition may not be the sole effect of eutrophication as it also implies an enhancement of organic matter fluxes to the vegetated sediments and therefore stimulating bacterial metabolism. Organic carbon inputs may induce sulfate reduction bacterial metabolism, which is the dominant biogeochemical process in coastal seagrass marine sediments (Jørgensen, 1982; Holmer et al., 2003) and is known to be particularly important for anaerobic organic carbon oxidation (Capone and Kiene, 1988; Howarth, 1993).

The end product of sulfate reduction, sulfide, has been identified as extremely toxic to plants (Terrados et al., 1999;

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Duarte, 2002). Its accumulation has been directly related to episodic die-offs of seagrasses such as *Thalassia testudinum* (Robblee et al., 1991; Carlson et al., 1994). Sulfide intrusion from the sediments into the plants, experimentally documented in *Zostera marina* (Pedersen et al., 2004) and in *T. testudinum* (Borum et al., 2005), has been recently proposed as a possible mechanism that may control the growth and survival of rooted plants in sulfate-rich aquatic environments (Borum et al., 2005).

A literature review suggested a threshold level of 100 μM (400–1000 μM) sulfide in sediment porewaters above which, seagrass growth would be impaired (Terrados et al., 1999). However, concentrations as high as 10 mM have been documented (Carlson et al., 1994, 2002), indicating that porewater sulfide concentrations vary widely among seagrass beds and that the resistance and tolerance to its accumulation varies among seagrass species and sediment biogeochemistry characteristics.

The biogeochemical pathways of sulfide porewater removal are still to be understood. Two mechanisms exist to counteract sulfide toxicity under seagrass beds. Firstly, seagrass roots and rhizomes supply oxygen to the sediment through photosynthesis maintaining an oxygen microshield surrounding them. This oxygen can support both biotic and abiotic reoxidation of reduced compounds such as sulfides, therefore preventing the rhizosphere to sulfide invasion (Pedersen et al., 2004). Secondly, the negative impacts of free sulfides can be also attenuated by the presence of sedimentary labile iron pools (Smolders et al., 1995; Viaroli et al., 1997) which can remove sulfide from porewater by precipitation as pyrite (FeS_2) and iron mono-sulfides (FeS), thereby acting as an alternative mechanism to sulfide detoxification and reducing its negative effects on seagrass growth. Therefore, low iron availability, which is characteristic of carbonate sediments (Berner, 1984; Duarte et al., 1995), limits the formation of iron-sulfide compounds and poorly buffer seagrass against dissolved sulfide toxicity (Chambers et al., 2001; Holmer et al., 2005).

Accordingly, it has been suggested that the seagrasses growing on carbonate sediments may be particularly prone to sulfide toxicity (Hemminga and Duarte, 2000), and recent experimental studies concluded that sulfides impact seagrass (*Posidonia oceanica*) growing on carbonate sediments at very low sulfide levels (20–30 μM, Holmer et al., 2003).

Despite the evidence that high sediment sulfide concentrations can have negative impacts on growth and survival of wetland plants and seagrasses (e.g. Havill et al., 1985; Bradley and Dunn, 1989; Koch and Mendelssohn, 1989), and that the sulfide removal by iron additions improve seagrass growth in impacted carbonate sediments (Chambers et al., 2001; Holmer et al., 2005), the direct links between growth conditions, invasion of sediment sulfide and subsequent shoot mortality have not yet been submitted to a comparable test. Several investigations have tried to establish clear relationships between sediment sulfide conditions and seagrass performance using different experimental approaches (e.g. Carlson et al., 1994; Goodman et al., 1995; Terrados et al., 1999; Erskine and Koch, 2000; Holmer and Bondgaard, 2001), but the experiments have produced highly variable results. This inconsistency could be explained by differences in the tolerance of various seagrass species to sulfide exposure, but also because of the complex nature of the interactions among the controlling factors, that makes reproducible and controlled experimental treatments hard to obtain (Terrados et al., 1999).

This study is addressed to test the hypothesized negative relationship between seagrass status and sulfide levels through a comparative analysis encompassing a range of seagrass meadows growing over carbonate sediments with variable sulfide porewater and organic carbon content levels. In order to be effective and to avoid confounding the results with species-specific responses or intrinsic differences in demographic rates across seagrass species, such comparative analysis has been referred to meadows of the same species.

The relationship between the status of *Posidonia oceanica* meadows and sulfide levels has been tested by the use of a comparative analysis of seven meadows spanning a range of conditions around the Balearic Islands, in the West Mediterranean Sea. We assessed organic matter contents, sulfate reduction rates and sulfide porewater concentrations in the sediments, concurrently with the assessment of demographic dynamics (specific mortality and net population growth rates) using repeated census of tagged plants.

2. Methods

The study was conducted at Mallorca Island and Cabrera Archipelago National Park (39°9' N, 2°56' E), a protected marine area, where a total of seven *Posidonia oceanica* meadows, selected on the basis of a broad survey of plant status, were sampled. *Posidonia oceanica* forms thick mats of rhizome and root material that occupy a substantial fraction of the sediment volume (Hemminga and Duarte, 2000). Study sites comprise a range of conditions from relatively pristine meadows (e.g. Magalluf and Sta Maria) to highly disturbed meadows (e.g. Sa Paret and Pollença, Table 1), growing on carbonate (>90% of dry weight, Holmer et al., 2003) sediments. Two sites in Mallorca (Magalluf and Cala Millor) were located in exposed areas, whereas two other sites (Porto Colom and Pollença) were in rather sheltered bays with relatively high nutrient loading. At Cabrera Island two sites (Es Castell, Sa Paret) were studied in a rather enclosed bay and one additional site (Sta Maria) in a more exposed bay, which is environmentally protected from human activities, with no public access. The meadows extend from near the surface (4 m depth, Pollença) down to 20 m (Es Castell), well above the 35 m depth limit of the plants (Table 1). Sulfate reduction rates and sulfide porewater concentrations had been investigated in some of these meadows in 2000–2001, as part of an earlier, exploratory study (Holmer et al., 2003) ranging from 0.7 to 12 mmol m^{-2} d^{-1} and from 0.1 to 29.5 μM, respectively. Impacts on the sediments derived from excess organic matter inputs from domestic sources, and the study sites did not receive industrial or substantial agricultural inputs. Seagrass status was characterized by shoot demographic dynamics, specifically the specific mortality and net population growth rates