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Assessment of the abiotic and biotic effects of sodium metabisulphite pulses discharged from desalination plant chemical treatments on seagrass (*Cymodocea nodosa*) habitats in the Canary Islands

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ABSTRACT

Reverse osmosis membranes at many desalination plants are disinfected by periodic shock treatments with sodium metabisulphite, which have potentially toxic effects to the environment for marine life, although no empirical and experimental evidence for this is yet available. The aim of this study was to characterise for the first time, the physico-chemical modification of the marine environment and its biological effects, caused by hypersaline plumes during these membrane cleaning treatments. The case study was the Maspalomas II desalination plant, located in the south of Gran Canaria (Canary Islands, Spain). Toxicity bioassays were performed on marine species characteristic for the infralittoral soft bottoms influenced by the brine plume (*Synodus synodus* and *Cymodocea nodosa*), and revealed a high sensitivity to short-term exposure to low sodium metabisulphite concentrations. The corrective measure of incorporating a diffusion system with Venturi Eductors reduced nearly all the areas of influence, virtually eliminating the impact of the disinfectant.

1. Introduction

Brine discharges from desalination plants where the discharge system lacks a high initial dilution capacity become hypersaline plumes with very high salinities and a high degree of stratification, making the exchange and dilution processes very slow (Palomar and Losada, 2008). As a result, brine discharges spread out over large areas of the sea floor (Fernández-Torquemada et al., 2009), following the steepest gradients (Payo et al., 2010), and with a high potential to alter the structure and distribution of benthic communities (Morton et al., 1996; Einav et al., 2002; Ruiz, 2005; Palomar and Losada, 2008). Brine effluents have been shown to cause adverse effects on benthic infaunal communities and fishes (Fielder et al., 2005; Miri and Chouikhi, 2005; Del-Pilar-Ruso et al., 2007, 2008, 2009; Castriota et al., 2001; Riera et al., 2011) and seagrass habitats (Fernández-Torquemada and Sánchez, 2005; Gacia et al., 2007). The extent and magnitude of such impacts ultimately depend on many factors related to the vulnerability of the benthic assemblages and their conservation status, prevailing environmental characteristics (bathymetry, climate and oceanography) and characteristics of the brine discharge, its chemical composition and the discharge system (Höpner and Widemberg, 1996; Einav et al., 2002; Fernández-Torquemada et al., 2009; Ruiz, 2005).

Seagrass meadows are dominant habitats of infralitoral environments of the Spanish Mediterranean and Atlantic coasts up to 30–40 m in depth, with *Posidonia oceanica* (L.) Delile and *Cymodocea nodosa* (Ucria) Ascherson being the most abundant and ecologically relevant species (Procaccini et al., 2003). These benthic habitats and the communities they contain are particularly vulnerable to the effects of human impact (Boudouresque et al., 2009), which motivated the first scientific projects that aimed to establish the adequate criteria to avoid, minimise and monitor the effects of brine effluents on marine environments (Sánchez-Lizaso et al., 2008). In the Mediterranean Sea, most of this initial research was dedicated to the endemic, dominant species, *P. oceanica*. This is a typical stenohaline species with a high sensitivity to chronic salinity increase, as demonstrated by diverse studies based on

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different field and laboratory experimental approaches (Fernández-Torquemada and Sánchez, 2005; Gacia et al., 2007; Ruiz et al., 2009). More recently, the stress-response mechanisms induced in this seagrass species by hypersaline conditions have been studied (Marín-Guirao et al., 2011; Sandoval-Gil et al., 2012a). Similar studies have been also performed with *C. nodosa*, a more euryhaline seagrass species with a broader ecological and geographical distribution than *P. oceanica* (Drew, 1978; Procaccini et al., 2003). Accordingly, the available evidence indicates a higher capacity of this seagrass species to tolerate chronic salinity increases (Pagés et al., 2010; Fernández-Torquemada and Sánchez Lisazo, 2011), due to specific physiological adaptations to cope with hypersaline stress (Sandoval-Gil et al., 2012a, b; Marín-Guirao et al., 2013).

However, very few studies have considered other factors than salinity that might explain the deleterious effects of brine effluents on seagrass communities (Fernández-Torquemada and Sánchez, 2003). One of these factors is the addition of diverse chemical products (anti-fouling agents, coagulants, acidifiers, disinfectants, etc.), the presence of which is usually considered sporadic and of little importance, although presumably with a high potential to cause persistent toxic effects on marine organisms (Sánchez-Lizaso et al., 2008). Sodium metabisulphite ($Na_2S_2O_5$; herafter, SMBS) is among the most common chemical additives used in shock or continuous cleaning treatments of reverse osmosis membranes. During the shock treatments, the product is applied periodically, so that its presence (and its sub-products) in the brine appears as a short-term pulse (minutes to hours) at a weekly frequency. The SMBS reacts with the oxygen dissolved in the water, releasing the gas sulphur dioxide (SO_2), which combines readily with water and results in an increase in the level of acidic substances (HSO_3^- as H_2SO_4; Singh and Singh, 1984). As well as the residues produced by the chemical reactions between the product and the brine (Na_2SO_3, CaSO, $CaSO_4$; Medina, 1999), its dissociation products alter the physico-chemical properties of the medium, leading to acidification (pH < 5) and hypoxia (dissolved oxygen saturation <5% DOsat). Such conditions are extremely adverse for the development and survival of benthic marine life (Singh and Singh, 1984; Galli et al., 2012; Figueiredo et al., 2006; Macintosh and Phillips, 1992; Silva 1988) and therefore are highly likely to significantly alter the structure and distribution of benthic habitats and communities. Nonetheless, to date, no studies are available concerning the effects of these chemical products present in brine effluents on any marine benthic community.

The aim of this study was to characterise for the first time, the physico-chemical modification of the marine environment, and the biological effects caused by hypersaline plumes during the operation of membrane cleaning treatments using SMBS. To this end, a location on the island of Gran Canaria (Canary Islands, Spain) was selected, where the spread of a brine discharge delivered by a desalination plant has been well characterised in previous studies in relation to different hydrodynamic conditions (Portillo et al., in press). Furthermore, this locality is an area of special conservation interest due to the presence of the most extensive and ecologically relevant *C. nodosa* seagrass meadow on the island. However, results from these previous studies showed that *C. nodosa* was absent in most of the area affected by the hypersaline plume, associated with the brine effluent. In this study, we evaluated the hypothesis that environmental modifications caused by salinity increases and SMBS additions associated with the brine effluent might be potential causes for the disappearance of the seagrass and its associated community in the area of influence of the effluent. To evaluate this hypothesis, a detailed spatial characterisation of physico-chemical variables (salinity, pH and DOsat) was initially performed, to assess the extent of environmental alterations caused by the brine discharge in the area. Secondly, various bioassays were performed to experimentally assess the potential effects of increases in salinity and SMBS-induced physico-chemical alterations on the vitality and survival of *C. nodosa* and on other key component characteristics of this benthic community, such as the predator Lizard fish, *Synodus synodus*. Thirdly, after the incorporation of a diffusion system with Venturi Eductors as a corrective measure, their ability to minimise the effects of such discharge during cleaning membrane operations using SMBS additions was evaluated.

2. Materials and methods

2.1. Study area and brine discharge

The studied brine discharge was delivered from the reverse osmosis desalination plant Maspalomas II, located in the South of Gran Canaria Island (Canary Islands, Spain; Fig. 1). The discharge was initiated in 1988 and, at the time of this study, it had a brine flow of 1062 m3/h with a salinity of 69.5 psu. Shock treatment to clean the reverse osmosis membranes is applied weekly to feedwater in the storage tank after it has been pumped from the marine environment and filtered. SMBS (1225 kg) is added to this tank every 45 min and enters the membrane system with a concentration of ca. 800 ppm. After the osmosis process, the product is delivered into the sea with the brine through a pipeline (300 m length and a 600 mm diameter) at a concentration of ca. 1, 600 ppm. The discharge point is at a depth of 4 m at mean low water spring tide (MLWS) and discharges over sedimentary bottoms with a slope of 1.6% and dominated by a large, patchy C. nodosa seagrass meadow of recognised ecological importance for the island (Special Conservation Zones of the UE Nature 200 network; BOE, 2009). The distribution of the C. nodosa meadows in the study area is shown area is shown in Fig. 1, together with the mean spatial spread of the hypersaline plume under low hydrodynamic exposure obtained in previous studies in this area (Portillo et al., in press). A discontinuity in the seagrass distribution at the level of the discharge point and the adjacent areas influenced by the hypersaline plume was appreciated. In 2012, a new discharge system with Venturi Diffusers was installed in the final end of the pipeline to allow a higher and more efficient dilution of the brine and to minimise its effect on the marine environment (Portillo et al., 2013). After the installation of the Venturi Eductors, it was observed that the salinities of the discharge zone almost equalled normal ambient salinity values for this coastal area, although modifications of other seawater physico-chemical characteristics are unknown, particularly during cleaning membrane operations using SMBS additions.

2.2. Field sampling for spatial characterization of physico-chemical variables

Before the realisation of the extensive sampling campaigns, three YSI-6600-V2 sondes were deployed on the seabed for 6 h to obtain continuous recordings of pH and near-bottom dissolved oxygen (DOsat, %) values at fixed positions located 0, 250 and 700 m from the discharge point (Fig. 3). The objective of this was to precisely characterise the temporal evolution of the above-mentioned variables in these locations, following the addition of SMBS, to obtain some basic information necessary for the design of sampling campaigns and bioassays. We specifically needed to determine (a) the duration of the exposure to deoxygenation and acidification conditions once the brine arrived at a particular point and (b) the velocity of the displacement of SMBS subproducts as the brine spread over the seabed.

Two sampling campaigns were performed for the spatial characterisation of physico-chemical characteristics of the brine