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Domoic acid in a marine pelagic food web: Exposure of southern right whales *Eubalaena australis* to domoic acid on the Península Valdés calving ground, Argentina

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ABSTRACT

The gulfs that surround Península Valdés (PV), Golfo Nuevo and Golfo San José in Argentina, are important calving grounds for the southern right whale *Eubalaena australis*. However, high calf mortality events in recent years could be associated with phycotoxin exposure. The present study evaluated the transfer of domoic acid (DA) from *Pseudo-nitzschia* spp., potential producers of DA, to living and dead right whales via zooplanktonic vectors, while the whales are on their calving ground at PV. Phytoplankton and mesozooplankton (primary prey of the right whales at PV and potential grazers of *Pseudo-nitzschia* cells) were collected during the 2015 whale season and analyzed for species composition and abundance. DA was measured in plankton and fecal whale samples (collected during whale seasons 2013, 2014 and 2015) using liquid chromatography coupled to tandem mass spectrometry (LC–MS/MS). The genus *Pseudo-nitzschia* was present in both gulfs with abundances ranging from 4.4×10^2 and 4.56×10^5 cell l^{-1}. *Pseudo-nitzschia australis* had the highest abundance with up to 4.56×10^5 cell l^{-1}. DA in phytoplankton was generally low, with the exception of samples collected during a *P. australis* bloom. No clear correlation was found between DA in phytoplankton and mesozooplankton samples. The predominance of copepods in mesozooplankton samples indicates that they were the primary vector for the transfer of DA from *Pseudo-nitzschia* spp. to higher trophic levels. High levels of DA were detected in four whale fecal samples (ranging from 0.30 to 710 $\mu g\, g^{-1}$ dry weight of fecal sample or from 0.05 and 113.6 $\mu g\, g^{-1}$ wet weight assuming a mean water content of 84%). The maximum level of DA detected in fecal samples (710 μg DA g^{-1} dry weight of fecal sample) is the highest reported in southern right whales to date. The current findings demonstrate for the first time that southern right whales, *E. australis*, are exposed to DA via copepods as vectors during their calving season in the gulfs of PV.

1. Introduction

Phycotoxins are secondary metabolites produced by certain species of phytoplanktonic microalgae. These toxic microalgae are consumed and their toxins bioaccumulated in organisms such as fish, molluscs, krill, copepods and other pelagic invertebrates (Carreto et al., 1986; Shumway, 1990; Turriff et al., 1995; Bagøien et al., 1996; Teegarden and Cembella, 1996; Hwang and Tsai, 1999; Lincoln et al., 2001; Tester et al., 2001; Bargu et al., 2002; Lefebvre et al., 2002, 2012; Costa et al., 2004) which act as transmission vectors. As a result, adverse effects of phycotoxins have been recorded in top predators such as sea birds (Fritz et al., 1992; Work et al., 1993; Beltran et al., 1997; Gayoso and Fulco, 2006), sea lions (Lefebvre et al., 1999, 2010; Scholin et al., 2000; Buckmaster et al., 2014), whales (Geraci et al., 1989; Fire et al., 2010; Lefebvre et al., 2016), dolphins (De La Riva et al., 2009; Lefebvre et al., 2016) and

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humans (Carreto et al., 1981; Perl et al., 1990; Mons et al., 1998) producing different types of gastrointestinal and neurological damage and even death.

Domoic acid (DA) is a potent water-soluble neurotoxin naturally produced by several species of the diatom genus *Pseudo-nitzschia*. This neurotoxin has been causative of many lethal incidents of marine mammals due to its transfer and accumulation through the trophic web via planktivorous vectors (Gulland, 1999; Lefebvre et al., 1999; Kreuder et al., 2005; Fire et al., 2010; De La Riva et al., 2009). Chronic exposure of sea lions to DA also produces sublethal effects, causing degenerative heart disease, chronic epileptic syndromes and reproductive failures through abortions, death in the uterus and premature parturition (Scholin et al., 2000; Brodie et al., 2006; Goldstein et al., 2009; Zabka et al., 2009). However, little is known about the effects of DA in baleen whales, such as right whales. It has been suggested that concentrations of DA that are not lethal in humans and monkeys, can cause symptoms of intoxication in whales that could lead to their death through chronic exposure in multiple feeding events (Fire et al., 2010).

Studies conducted in the northern hemisphere have demonstrated that North Atlantic right whales (*Eubalaena glacialis*) are exposed to DA mainly through the calanoid copepod *Calanus finmarchicus*, a primary prey in their spring and summer feeding areas along the northeastern US and eastern Canadian coasts (Leandro et al., 2010a; Doucette et al., 2012). Likewise, DA was detected in fecal samples of blue whales (*Balaenoptera musculus*) and humpback whales (*Megaptera novaeangliae*) during a toxic bloom of *P. australis* in Monterey Bay, California (Lefebvre et al., 2002). Similarly, trace levels of DA were detected in tissues (Rowntree et al., 2013) and blood samples (Wilson et al., 2015) collected from dead southern right whales (*Eubalaena australis*) that stranded at Península Valdés (PV). In addition, recent studies have documented the presence of frustule fragments of *Pseudo-nitzschia* spp. potentially producing DA as well as microcrustacean remains, mainly copepodite 5 mandibular gnatobases of *Calanus australis* (a common species in Argentine Sea), in fecal samples of living and dead whales from the Nuevo (GN) and San José gulfs (GSJ) respectively (D'Agostino et al., 2015, 2016). These findings indicate that southern right whales could be exposed to DA while feeding in the area and copepods could have act as a primary vector of this neurotoxin. However, the transfer of DA from the toxic phytoplankton to southern right whales through zooplankton vectors has not been studied previously.

The gulfs of PV, GSJ which opens to the north and GN which opens to the south (Fig. 1) are important calving grounds for the southern right whale population in the western South Atlantic Ocean. The whales arrive at PV in late austral fall and remain in the area during the winter and spring months where they reproduce and give birth to their calves. In spring, as denser zooplankton patches follow the spring phytoplankton blooms, adults and juveniles begin to filter zooplankton (mainly copepods) by skimming-feeding at the sea surface or by diving to greater depths (Sironi, 2004; Menéndez et al., 2007; Hoffmeyer et al., 2010; D' Agostino et al., 2016). Previous studies confirm that spring phytoplankton blooms in both gulfs are dominated by diatoms with *Pseudo-nitzschia*, in some cases being the most abundant genus (Gayoso, 2001; Sastre et al., 2007; Cadaillón, 2012). Therefore, the feeding of southern right whales in GN and GSJ show a certain degree of temporal overlap with the potentially toxic *Pseudo-nitzschia* blooms occurring in the area during spring.

In the PV calving ground, the population of southern right whales has been increasing at a rate of between 4.57 and 6.2% annually during the last 15 years (Crespo et al., 2014). However, in recent years the population experienced a series of high mortality events with 753 dead whales recorded from 2003 to 2016, 91% being calves (report Southern Right Whale Health Monitoring Program [SRWHMP]; 2003–2016). The effect of phycotoxins on the health of the southern right whale was suggested as a possible explanation for the high mortality events (Rowntree et al., 2013; Wilson et al., 2015). In this region, the transfer of DA from the phytoplankton to zooplankton has been previously documented (Cadaillón, 2012). However, knowledge about the levels of DA to which whales are exposed while at PV area and the potential vectors of this potent neurotoxin is still incipient. In this context,

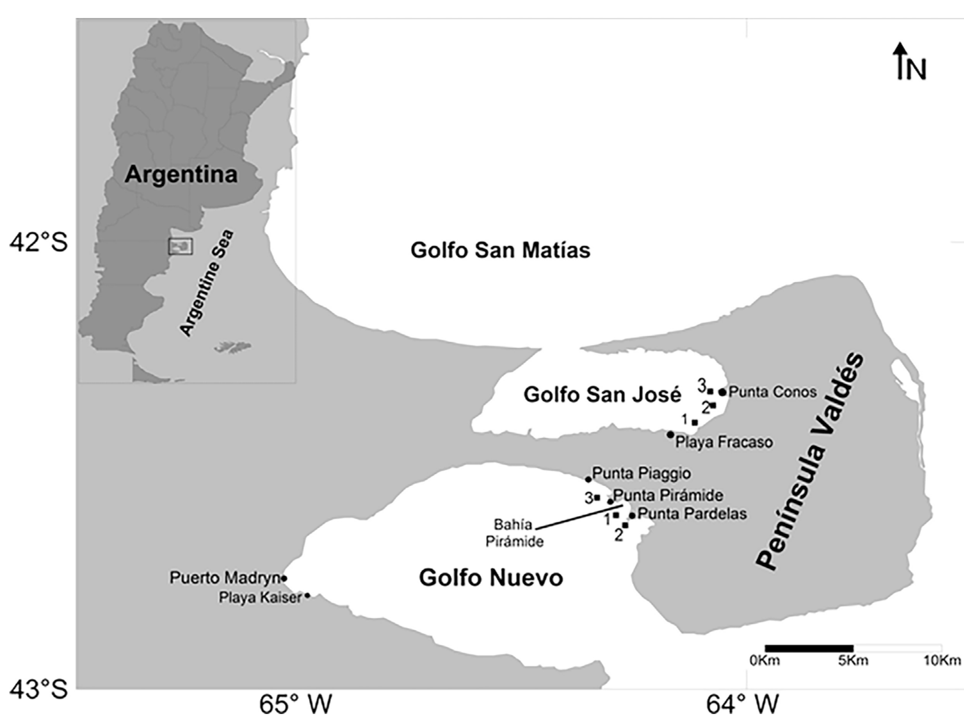

Fig. 1. Study area showing the location of sampling sites in Golfo Nuevo and Golfo San José, Península Valdés, Argentina.