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Characterisation and preliminary quantification of the methane reservoir in a coastal sedimentary source: San Simón Bay, Ría de Vigo, NW Spain

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ABSTRACT

Ría de Vigo is a river valley flooded by the sea, with a bay (San Simón Bay) at its innermost part. The accumulation of Holocene sediment in San Simón Bay has been studied by the integration of 1) large scale high resolution seismic data, and 2) detailed geochemical analysis of a gravity core. In San Simón Bay the majority of the seismic records are obscured by acoustic turbidity which represents gassy sediments, but on records from Rande Strait it is possible to distinguish two Quaternary seismic sequences; an Upper Pleistocene sequence (SQ1) and a Holocene sequence (SQ2). Only SQ2 is recognized in San Simón Bay where it is comprised of two seismic units; the upper unit represents the HST sediment, i.e. the period of highest sea level. A gravity core taken within the gassy zone at 10 m water depth provided 3.55 m of fine-grained sediments (muds) from the youngest seismic unit (4 m thick). Geochemical analysis show high values (4 to 10%) of TOC. Sediment and porewater analyses indicate a distinct sulphate–methane transition zone (SMTZ) between 60 and 80 cm where sulphate is depleted (to <1.7 mM) and methane increases (to >0.4 mM). The top of the acoustic turbidity (the gas front) at 80 cm corresponds to the lower limit of the SMTZ. The methane cannot have been derived from the underlying metamorphic and granitic rocks, but was probably derived by microbial degradation of the organic matter in the Holocene sediments. We estimate that the sediments of the Bay contain approximately 1.8×10^6 m^3 of organic carbon and 275 ton of methane.

1. Introduction

Modern continental shelves contain substantial amounts of methane, predominantly produced through microbial degradation of organic matter (e.g. Martens and Berner, 1974; Hovland and Judd, 1992; Fleischer et al., 2001; Judd and Hovland, 2007 etc.). Although the total mass of methane in sediment beneath shallow marine waters has not been quantified (Fleischer et al., 2001), methanogenesis probably occurs over at least 30% of the world's continental shelves (Hovland and Judd, 1992). Estimates of the annual CH_4 flux from marine seeps to the atmosphere vary (see EPA, 2010, for a detailed discussion), for example: Hornafius et al. (1999) estimated a flux of 18–48 Tg whilst, Kvenvolden and Rogers (2005) suggested a flux of 10–30 Tg. EPA (2010) reported 0.5–9.7 Tg from the continental shelves and a further 1.06–2.1 Tg from estuaries. There are, however, significant uncertainties in these estimates. Current estimates do not include emissions from upwelling areas. Perhaps unsurprisingly, emissions appear to be dominated by coastal and shelf systems, where organic sources are greater and contact with anaerobic sediments is greater.

Work on coastal shelves and in estuaries indicates that these areas likely dominate the marine CH_4 cycle, prompting re-evaluations of the role of marine waters in the global budget (e.g. Bange et al., 1994; Upstill-Goddard et al., 2000). Kitidis et al. (2007) estimated that $18–44 \times 10^6$ g ($1.1–2.7 \times 10^6$ mol) CH_4 is emitted to the atmosphere CH_4 from the Ría de Vigo. This is 2 orders of magnitude lower than a previous estimate of $0.1–4.1 \times 10^9$ g year^{-1} for CH_4 ebullition fluxes based on the density of acoustic plumes and pockmarks (García-Gil et al., 2002), and is comparable to the annual sea–air flux of CH_4 from the UK's Humber estuary (36×10^6 g year^{-1}, Upstill-Goddard et al., 2000). In shallow nearshore regions such as the Ria de Vigo bubble residence times in the water column may be very short.

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Consequently, rising bubble plumes may provide significant quantities of CH_4 to the atmosphere which remain unaccounted by flux estimates that are based on dissolved gas distributions alone.

Rias are drowned fluvial valleys that have been partially infilled with relatively young sediments. Over recent years detailed mapping of the Rías Baixas (Arousa, Pontevedra and Vigo) in northwest Spain, has shown that they all have extensive acoustic turbidity in the Holocene fill-sediments, indicating shallow gas accumulations and acoustic plumes or seabed features (such as pockmarks) associated with gas escape (García-García et al., 1999, 2003; García-Gil et al., 2002; García-Gil, 2003). Sampling and analysis of gas bubbles in the water column from San Simón Bay confirmed that the gas was methane (García-Gil, 2003; Iglesias and García-Gil, 2007; Kitidis et al., 2007).

Sedimentary records from the rias provide excellent opportunities to evaluate the stratigraphic context of shallow gas accumulations, with particular respect to sea level changes during the Quaternary. Detailed stratigraphy of Ría de Vigo has shown that the drowned valley was cut into ancient rocks (Palaeozoic metamorphics and granites) which are most unlikely to be sources of methane (García-Gil et al., 1999; García-Gil, 2003). During the last glacial maximum it was an incised valley, and sediments which infill this valley were deposited during last sea level rise. These young sediments are characterised by high concentrations of organic carbon; conditions are suitable for microbial methane generation, and the sediment record also offers important information about the biogeochemical cycles that involve the transformation of sediments and organic matter. Methanogenesis commenced shortly after the organic matter was deposited and occurred mainly at relatively shallow depths within sediments in which sulphate levels have been depleted by the activities of sulphate-reducing bacteria. Where concentrations of reactive organic carbon are high enough, methane concentrations can rise to exceed methane solubility, permitting the formation of gas bubbles (Schubel, 1974; Abegg and Anderson, 1997; Whiticar, 2002).

Therefore, considering the discrepancies and uncertainties related to the methane fluxes from these shallow marine environments, it becomes very relevant to quantify the total mass of methane in sediment beneath the shallow marine waters of San Simón Bay that potentially can escape to the water column and to the atmosphere. The quantification of total organic carbon as well as the methane stored in this shallow gas field constitutes the first step for a more accurate methane budget based.

The importance of studying shallow gas accumulations lies in the assessment of their impact on the global environment and their effects on human activities in the marine environment. Drops in hydrostatic pressure can trigger sudden ebullition of the greenhouse gas methane from the seafloor into the atmosphere, and also, the presence of shallow gas modifies the geotechnical properties of sediments, altering their strength (Anderson and Hampton, 1980; Sills and Wheeler, 1992; Judd and Hovland, 2007 etc.).

The objective of this paper is to provide a preliminary characterisation of the gassy sediments of San Simón Bay. Specifically, to identify the sequence of events culminating in the generation of methane within the sediments; to delimit the area of gassy sediments; to characterise the sediments in which methane is generated and accumulated; and to estimate the quantity of methane held with the sediments. These objectives have been addressed by a combination of seismic stratigraphy applied to high resolution seismic data, and geochemical analyses of core samples. The ria is an ideal location (or place) to study the generation, migration and escape of methane to the hydrosphere and atmosphere of methane. San Simón Bay, the innermost part of the Ría de Vigo, is particularly suitable for this study because of its shallow (<20 m) water, and the restricted age of the sediments.

2. Environmental setting/geological framework

2.1. Physiography and oceanography

The Ría de Vigo, in the northwest Iberian Peninsula, is a large submerged, incised valley which is orientated SW–NE (Fig. 1). San Simón Bay is a small N–S-orientated shallow basin located in the innermost part of the ria. It is 10 km long and 4 km wide, and covers an area of 19.5 km^2. The bay is connected to the ria by a narrow channel, Rande Strait which is 600 m wide and 1.5 km long. The present seabed gently slopes to the SW. The water depth increases from 20 m in the entrance to the bay, to 35 m in the strait in a distinct step or sill.

Along-shore winds interact with the coastal topography to generate upwelling-downwelling dynamics on the continental shelf which drive the ria's water circulation pattern (Fraga, 1981; Doval et al., 1997; Alvarez-Salgado et al., 1999; López et al., 2001; Figueiras et al., 2002; Gago et al., 2003; Souto et al., 2003). The intrusion of nutrient-rich coastal waters at the seabed increases productivity in the ria, and is associated with the enhancement of the flow of organic matter (OM) towards the seafloor.

Average salinity decreases from 36‰ in the outer part of the ria to 31–32‰ at the entrance of San Simón Bay. Lower salinity values are found in the river estuaries in the bay. The most significant fresh water input to the ria comes from several relatively small rivers which flow into San Simón Bay, where estuarine conditions are enhanced. Average fluvial discharge to the bay is 20 m^3 s^{-1} (Nombela et al., 1995; Pérez-Arlucea et al., 2005), which represents 75% of the total fresh water input to the ria. The major water input is located at the northern end of the bay, with 18.2 m^3 s^{-1} mean total discharge and 4 mg l^{-1} of suspended sediment concentration coming from three rivers; the SE area is drained by a single river which discharges at 0.9 m^3 s^{-1} with 225 mg l^{-1} of suspended load. During periods of high river discharge, particularly in spring, vertical salinity gradients develop whereby a thin surface layer of low salinity water extends seawards of the RandeStrait into the main ria. Superficial water temperatures vary from 11 to 12 °C in winter to 19 to 20 °C in summer.

San Simón has a 2.2 m medium tidal range (i.e. it is mesotidal). Current measurements from the surface and bottom in the centre of the bay indicate velocities of 35 and 18 cm/s, respectively (Nombela et al., 1995). Therefore, the sedimentary environments in the bay are largely controlled by tidal processes. Intertidal areas cover 7.2 km^2 and are developed mainly in the middle-northern part of the bay where there are important marshes, sandy intertidal flats, estuarine–deltaic complexes, beaches and muddy intertidal flats. Subtidal areas characterised by a predominance of muddy sediments extend over 12.3 km^2. These sediments are the richest in organic matter found in the superficial sediments of the ria, with contents ranging from 7 to 10% (Vilas et al., 1995). Coarse-grained sediments (sand and gravels) are found only close to the river mouths.

2.2. Underlying geology

The Galician coastal area is characterised by granites and by Palaeozoic sedimentary rocks that have been metamorphosed by compression and heating. These rocks constitute the 'basement'. The structural history of this area has resulted in major faulting, and the orientation of the ria and the bay suggest that their formation, probably during the Miocene if not more recently, was dictated by this structural fabric (García-Gil, 2003; García-García et al., 2005). Another important structural feature is a ridge (which includes a series of islands, the Cies Islands) which forms a partial barrier between the ria and the open Atlantic Ocean. This ridge exerts an