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Article

Determination of Priority Study Areas for Coupling CO_2 Storage and CH_4 Gas Hydrates Recovery in the Portuguese Offshore Area

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Abstract: Gas hydrates in sub-seabed sediments is an unexploited source of energy with estimated reserves larger than those of conventional oil. One of the methods for recovering methane from gas hydrates involves injection of Carbon Dioxide (CO_2), causing the dissociation of methane and storing CO_2. The occurrence of gas hydrates offshore Portugal is well known associated to mud volcanoes in the Gulf of Cadiz. This article presents a determination of the areas with conditions for the formation of biogenic gas hydrates in Portugal's mainland geological continental margin and assesses their overlap with CO_2 hydrates stability zones defined in previous studies. The gas hydrates stability areas are defined using a transfer function recently published by other authors and takes into account the sedimentation rate, the particulate organic carbon content and the thickness of the gas hydrate stability zone. An equilibrium equation for gas hydrates, function of temperature and pressure, was adjusted using non-linear regression and the maximum stability zone thickness was found to be 798 m. The gas hydrates inventory was conducted in a Geographic Information System (GIS) environment and a full compaction scenario was adopted, with localized vertical flow assumed in the accrecionary wedge where mud volcanoes occur. Four areas where temperature and pressure conditions may exist for formation of gas hydrates were defined at an average of 60 km from Portugal's mainland coastline. Two of those areas coincide with CO_2 hydrates stability areas previously defined and should be the subject of further research to evaluate the occurrence of gas hydrate and the possibility of its recovery coupled with CO_2 storage in sub-seabed sediments.

Keywords: gas hydrates; CO_2 storage; Portugal; seabed sediments; climate change mitigation

1. Introduction

Anthropogenic CO_2 emissions are pointed as the main driver of global climate change and its negative impacts in nature and society [1]. The energy demand is increasing in many regions of the world and particularly in developing countries, such as China, India and Brazil [2]. Increased energy efficiency and renewable energy sources are essential to reduce CO_2 emissions from energy production. However, for the coming decades it is unlikely that renewable energy sources will be able to cope with the rising energy demand, and fossil fuels will remain the main energy source. CO_2 Capture and Storage (CCS) is seen as a technology that could bridge the current fossil fuel based society to a low carbon future.

Geological storage of CO_2 generally focuses on saline aquifers, depleted oil and gas fields and the use of CO_2 for Enhanced Oil Recovery (EOR). Recent years have also seen an increased interest in CO_2 storage through *in situ* mineral carbonation in basalts. However, a less studied option available for those countries with a deep geological continental margin at close distance from shore is the storage of CO_2 in sub-seabed sediments in the form of hydrates, as proposed by Koide *et al.* [3] and Li *et al.* [4].

Bernardes *et al.* [5] defined three areas suitable for CO_2 storage in hydrates form in the Portuguese geological continental margin, at a distance of about 70 km from the coast and from the main CO_2 emission clusters in the country. However, that analysis also acknowledged the economic unfeasibility of that option, mainly due to the more than 1100 meters of water column required for the CO_2 hydrates stability in the Portuguese geological continental margin.

However, coupling CO_2 storage with methane recovery from gas hydrates can result in economic benefits. In that process, under the appropriate pressure and temperature conditions, gas hydrates are dissociated by CO_2 injection, releasing methane (CH_4) from the hydrates and replacing it by CO_2 molecules in the hydrate molecular cages.

In 2012, the first *in situ* test of CO_2 injection to dissociate gas hydrates and recover CH_4, was performed. During the field test, 6.11 Million cubic meters (Mm^3) of gas were injected, from which 4.74 Mm^3 of nitrogen (N_2) and 1.37 Mm^3 of CO_2. During the production phase, 24.21 Mm^3 of CH_4 were recovered with 70% and 40% of the previously injected N_2, and CO_2, respectively [6].

Several works based on geophysical, geochemical and geological data [7,8] have identified the occurrence of gas hydrates at more than 100 offshore sites around the world, including in the Gulf of Cadiz, just south from the Algarve coast in Portugal, where several mud volcanoes are known to hold gas hydrates [9–11].

An economically viable way to store CO_2 in seabed sediments, in its hydrate form, on the Portuguese geological continental margin could be to couple it with CH_4 recovering from gas hydrates. However, at present, there is no inventory of methane hydrates occurrences on Portugal's deep offshore.

Within this article, an estimate of the amount of CH_4 hydrates on the Portuguese geological continental margin is presented as a first step towards assessing the possibility of coupling CO_2 storage and CH_4 recovery. This article aims to define areas of possible formation of gas hydrates and their overlap with the CO_2 hydrates potential storage areas defined in Bernardes *et al.* [5] (Figure 1).

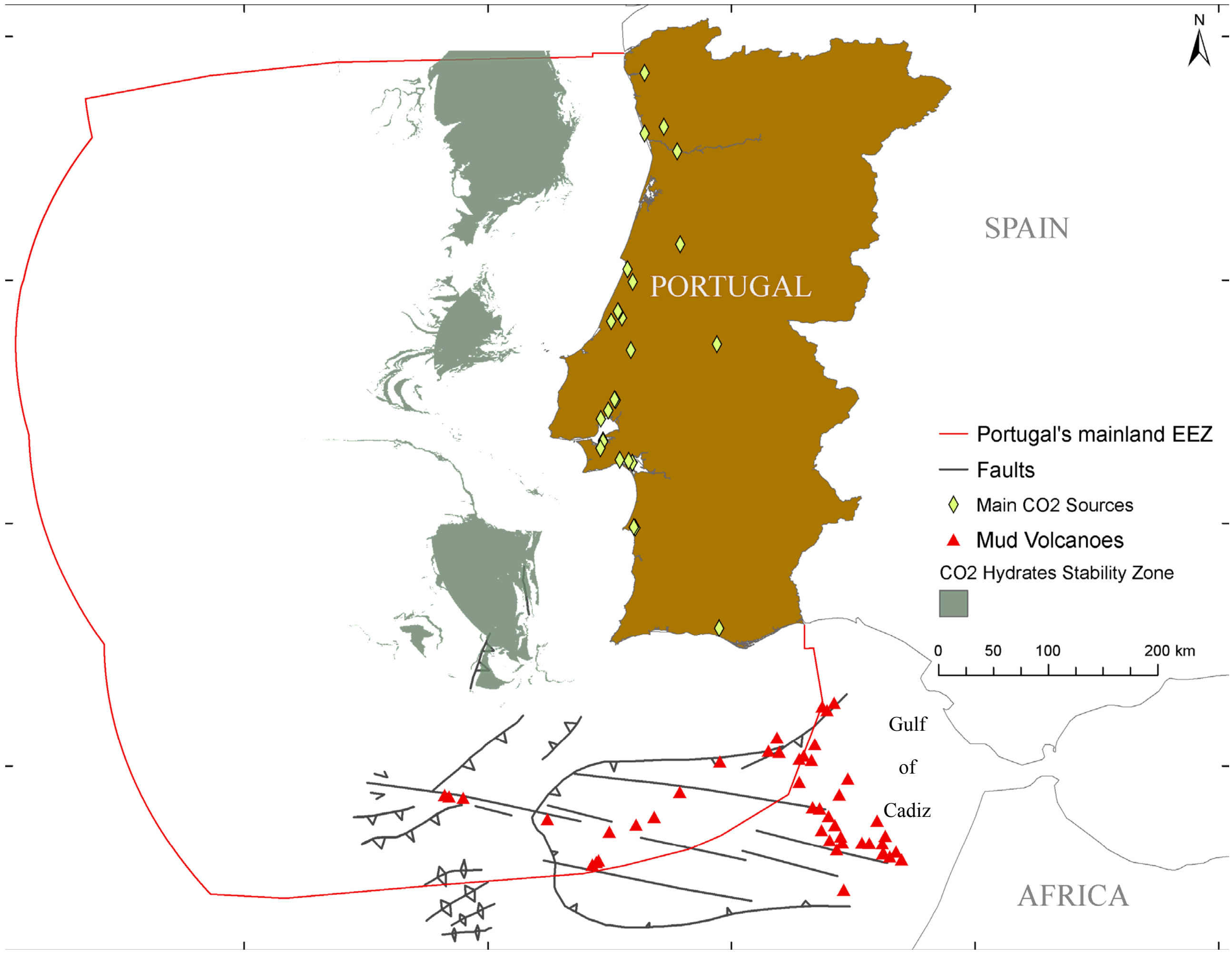

Figure 1. Location of the CO_2 hydrates stability zones defined in Bernardes *et al.* [5].

2. Background

Natural CH_4 hydrates occur and remain stable in sub-seabed sediments, mud volcanoes and other geological formations, under a specific range of pressure and temperature conditions. Thermodynamic calculations show that CH_4 hydrates are stable at relatively low-pressure (low water depths) conditions at typical seabed temperatures, as long as gas concentration is sufficient. Figure 2 depicts the methane hydrates stability conditions, according to several authors.

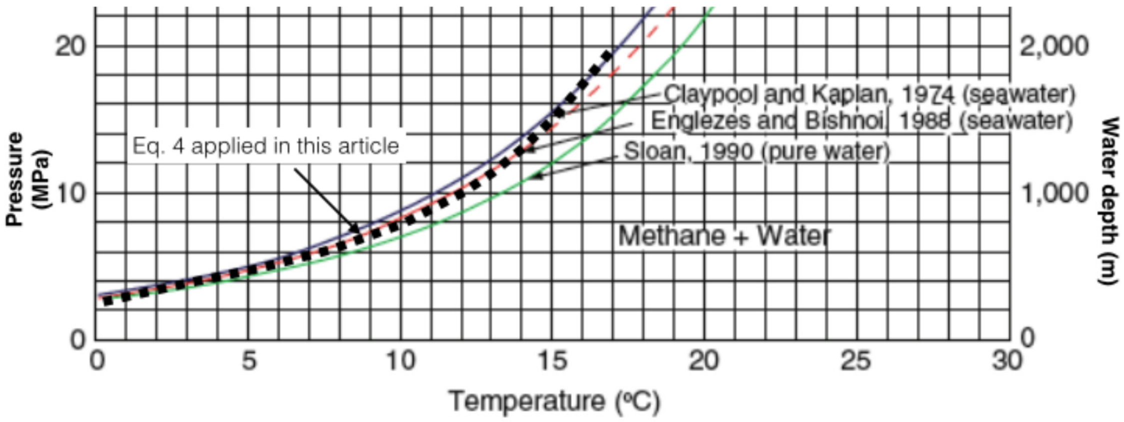

Figure 2. Gas hydrates phase boundary conditions, according to several authors (Adapted from Thakur [12]). Also depicted (dashed black line) the non-linear equation applied in this article.

Hydrates are polyhedral structures that form a cage composed by water molecules capable of retaining non-polar neutral guest gases. The interconnection of water molecules is strong since each molecule can donate and receive two hydrogen bonds. The stability of hydrates is only possible if more than 90% of the total cavities are fully filled by gas [13].

Due to chemical reactions, the decomposition of organic matter by anaerobic bacteria, at low temperature generates biogenic CH_4 [12]. When Sedimentation rates (S_r) and Particulate Organic Carbon (P_c) are higher than 1 cm/kyr and higher than 1%, respectively, anaerobic bacteria produces CH_4 few cm below the sea floor [12]. Kvenvolden *et al.* [14] defined the range of S_r from 3 to 30 cm/kyr to form biogenic CH_4. Collett [15] and Klauda and Sandler [16] have shown that hydrates do not form if P_c values are below 0.4% to 0.5%.

Hydrates formation is limited by a certain number of variables such as temperature-pressure pairs, organic matter availability, salinity, hydro and geothermal gradients and petrophysical conditions. Methane formation in ocean sediments is created by sulfur reduction and hydrogen sulphide release, from the upper parts of seafloor to hundreds of meters below. At larger depths, methane is produced by catagenesis, where temperature and pressure are the driving parameters [12].

Pore water salinity limits the capacity of the sediments to host gas hydrate and also lowers methane solubility. This leads to reduction of the amount of gas required for hydrates formation. Salinity causes two effects: it decreases the solubility of methane hydrates, but the existence of salts inhibits the formation of hydrate, increasing the dissociation pressure and methane concentration in the solution, although the solubility effect overweighs the effect of an increasing dissociation pressure [12].

Recent studies [17–19], estimate the global inventory of gas hydrates in marine sediments, taking the geological evolution, the sedimentation rate and the Particulate Organic Carbon data [19]. The Gas Hydrate Inventory (GHI) applied transfer functions derived from a numerical model developed by Wallmann *et al.* [18] simulating the gas hydrates formation under normal compaction and full compaction scenarios. The transfer functions, fitted by Piñero *et al.* [19], attempt to estimate the gas hydrates mass based on a reduced number of parameters, namely the sedimentation rate, the particulate organic content, vertical fluid flow and the thickness of the gas hydrates stability zone.

Equation (1) represents the transfer function for estimating the GHI in the full-compaction scenario [19] used to estimate values on Portugal's offshore.

$$GHI = b_1 L_{sz}^{b_2} \left(P_c \frac{b_3}{S_r^{b_4}} \right) \exp[-(b_5 + b_6 \ln[S_r])^2] \quad (1)$$

where L_{sz} is the thickness of hydrate stability zone, P_c is the particulate organic content, S_r is the sedimentation rate, and b_1 to b_5 are the transfer function fit parameters: b_1 = 0.00285, b_2 = 1.681, b_3 = 24.4; b_4 = 0.99, b_5 = −1.44 and b_6 = 0.393 [19].

The thickness of the gas hydrate stability zone (L_{sz}) depends on several parameters: bathymetry, geothermal gradient, temperature, pressure, gas concentration, salinity, porosity and permeability. For analysis at the regional scale, without considering the local variation of petrophysical quantities, the geothermal gradient, temperature/pressure pairs and water salinity are the crucial parameters. Pressure can be assimilated to hydrostatic pressure and readily estimated, while water salinity can be measured. Temperature and its variation with depth (*i.e.*, the geothermal gradient) vary with the geological conditions of the area in study and can be estimated based on bottom-hole temperature measurements in boreholes.

Regarding to geothermal gradient calculations, Piñero *et al.*, [19] compared two models published by Pollack *et al.* [20] and Hamza *et al.* [21]. They found Hamza *et al.* [21] models' to have a better match with Bottom Simulating Reflector (BSR) from Ocean Drilling Program (ODP) sites [22]. The maximum L_{sz} of 900 m was calculated with a thermal conductivity of 1.5 $Wm^{-1}\cdot K^{-1}$.

Leon *et al.* [23] applied a GIS model to estimate the L_{sz} in the Gulf of Cadiz, and retrieved a maximum thickness of 770 m for biogenic hydrates, with the expected BSR at around 800 m water depth.

Piñero *et al.* [19] also introduced vertical fluid flow (q) in the gas hydrate inventory, using Equations (2) and (3) for different ranges of vertical fluid flow. The fit parameters are the same as those ones published on [19].

For fluid flow:

$$q \geq 0.001 S_r (2 + \ln[P_c])$$

GHI is estimated from:

$$GHI_q = c_1 L_{sz}^{c_2} c_3 + \left(c_3 + \frac{1}{S_r} \right) (P_c + c_4 q^{c_5}) P_c^{c_6} \quad (2)$$

For fluid flow:

$$q < 0.001 S_r (2 + \ln[P_c])$$

GHI is estimated from:

$$GHI_q = GHI - 10^{-8} c_7 L_{sz}^{c_4} \left(1 + \frac{1}{S_r} \right) q P_c^{c_9} \quad (3)$$

Gas hydrates accumulation is inhibited when fluid flow is:

$$q > 1.3 \times 10^{-8} L_{sz}^2 S_r P_c$$

The transfer function coefficients in Equations (2) and (3) are c_1 = 0.024, c_2 = 1.587, c_3 = 0.0224, c_4 = 266084, c_5 = 2.75, c_6 = 0.063, c_7 = 0.003, c_8 = 4.68 and c_9 = 2.31 [19].

Piñero *et al.* [19] found in the Full Compaction scenario, hydrates are estimated to occur in areas larger volumes. If vertical fluid flow is also considered, the global amount of GHI is estimated at nearly 550 Giga ton of Carbon (GtC) [19].

The scenario with vertical fluid flow may be appropriate for, at least, part of our study area, namely the Gulf of Cadiz sector included in the Portuguese Economic Exclusive Zone (EEZ) (Figure 1). Geologically, the Gulf of Cadiz is located on a complex transpressive setting nearby the Africa-Eurasia plate boundary [24]. Mud volcanism in the Gulf of Cadiz is triggered by compressional stress related with the Africa plate WNW-ESE trajectory at a rate of about 4.0 mm/yr [5]. It is generally associated to fluid escape, along tectonic structures such as thrust faults, extensional faults, strike-slip faults and diapirs, that opens up pathways to over pressurized fluids, culminating on the formation of mud volcanoes [25,26]. Somoza *et al.* [27] suggested that shallow fluid upward flow could be originated by the perturbation of gas hydrates rich sediments by the Mediterranean Outflow Water (MOW). In any circumstance vertical fluid flow occurs and the gas hydrate inventory should consider the model given by Equations (2) and (3).

3. Methodology

The methodology implemented aimed to identify areas where biogenic gas hydrates are likely to be formed in the Portuguese geological continental margin and their overlap with areas defined by Bernardes *et al.* [5] as suitable for CO_2 storage in hydrates form in the subseabed sediments.

Two scenarios were considered based on the Piñero *et al.* [19] transfer-functions: (1) Assuming full compaction of the sediments at higher depth and (2) Full compaction of the sediments combined with vertical fluid flow on the Gulf of Cadiz. Piñero *et al.* [19] transfer function for the normal compaction scenario was also applied, but in that case there are no conditions for gas hydrates formation in the Portuguese geological continental margin.

The full compaction scenario favors hydrate formation due to the decrease in porosity and subsequent increase in CH_4 concentration within the pore water. The full compaction scenario also decelerates the loss of methane-rich pore fluids below the GHSZ, due to the increasing difference in burial velocity of pore water and bulk sediment [19]. The overburden load of younger sediments being continuously deposited on seabed drives sediment compaction by inducing an exponential decrease in porosity and water content with the sediment depth [18]. Upward fluid flow happens when sedimentary pressure gradient exceeds the hydrostatic pressure [18]. Full compaction may occur at the base of thick sedimentary deposits and in compressive tectonic settings, although the porosity of sediments usually is not completely eliminated by compaction [18]. Simulations by Wallmann *et al.* [18] show that GHI is significantly enhanced by Full Compaction scenario.

The methodology (Figure 3) was implemented in a GIS environment gathering data on the relevant features of the deep offshore, although the determination of the gas hydrate stability zone thickness (L_{sz}) was computed using a Fortran code, due to the non-linearity of the equations applied that cannot be easily implemented in a GIS environment.

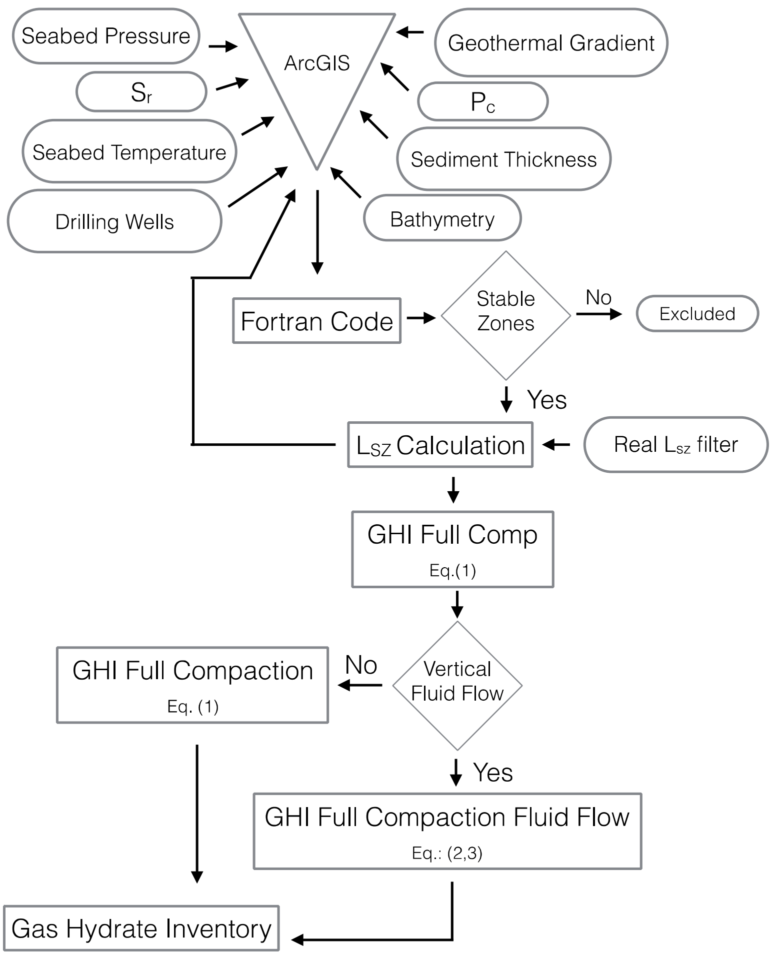

Figure 3. Methodology flow diagram.

The GIS includes data on bathymetry, hydrostatic pressure, temperature at the bottom of water column, oil exploration drilling wells, geothermal gradient, sediment thickness, accumulation of particulate organic carbon on the sea floor (P_c) and sedimentation rates (S_r), considered as steady state.

Raster datasets of seabed temperatures, hydrostatic pressure and sediment thickness for the study zone were the same used on Bernardes *et al.* [5]. The other datasets where built for this study and described in the next section.

4. Results and Discussion

4.1. Thickness of Gas Hydrates Stability Zone (L_{sz})

The determination of the GHSZ thickness (L_{sz}) depends on the thermodynamics of the gas hydrates boundary, namely pressure and temperature, and the inhibitor effect of water salinity. Since the equation that describe the thermodynamic behavior of hydrates is difficult to implement in a GIS, an approximation to the phase boundary computed by the *CSMHYD* code [28] was used, considering a seawater salinity of 36 g/L. Pressure and temperature dissociation pairs were found in *CSMHYD* to which a non-linear regression fitted the following function.

$$\frac{1}{T_{sf} + L_{sz}\delta_g} = \sum_{i=1}^{3} c_i \left[\log(L_{sz}\gamma_W g + P_{sf}\right]^{i-1} \quad (4)$$

where T_{sf} and P_{sf} are the seabed temperature and pressure, respectively, δ_g is the geothermal gradient, γ_w is the sub-seabed formation water salinity (assigned as 3.6% weight), g is gravity and c_i are the non-linear regression factors $c_1 = 3.8 \times 10^{-3}$, $c_2 = -4.09 \times 10^{-4}$ and $c_3 = 8.64 \times 10^{-5}$.

The phase boundary approximation (Equation (4)), is represented in Figure 2 and implemented in a Fortran code, *CO2hydrate*, coupled with the GIS model. The raster datasets of geothermal gradient (δ_g), seafloor pressure (P_{sf}) and seafloor temperature (T_{sf}) used in *COHydrate* are shown in Figure 4 and were derived by Bernardes *et al.* [5], although the geothermal gradient dataset was updated using data listed in Benazzouz [29].

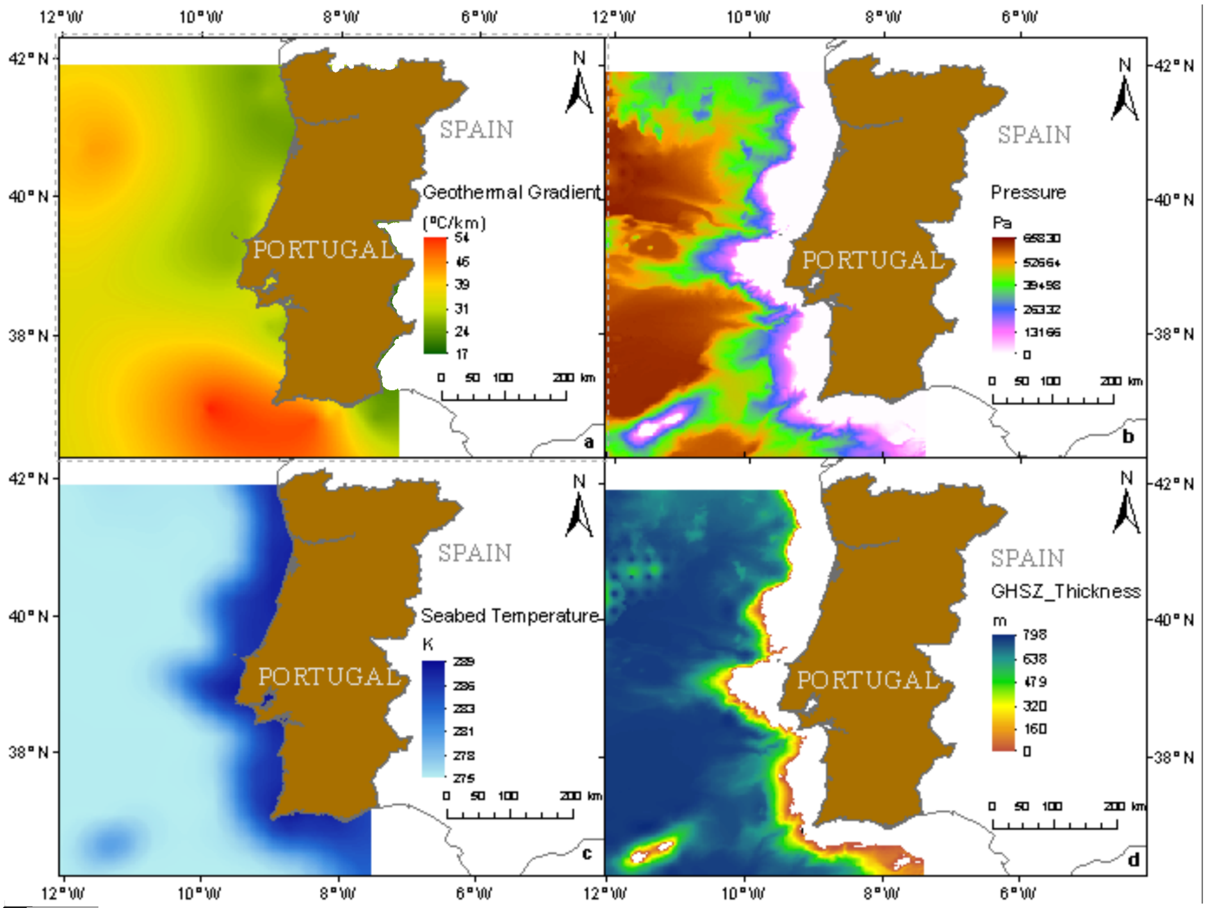

Figure 4. Raster datasets. (**a**) Updated geothermal gradient; (**b**) Hydrostatic pressure; (**c**) Seabed temperature; (**d**) GHSZ thickness (L_{sz}).

The maximum L_{sz} thickness of 798 m (Figure 4d) was found to be in agreement with the values computed by Leon *et al.* [23], and by Peter R. Miles (725 m) as quoted by [29], but contrasts with the 550 m depth estimated by Benazzouz [29].

According to the model implemented, the L_{sz} is highly influenced by the high seawater temperatures in the Portuguese offshore, and it shows that gas hydrates could be stable at depths varying from 600 m to 3000 m. The minimum depth required for GHSZ is 600 m, much shallower than the 1100 m minimum depth for the CO_2 hydrates stability zone computed by Bernardes *et al.* [5]. Thus, for the purpose of this paper, only the GSHZ occurring deeper than 1100 m and overlapping with the CO_2 hydrates stability zones is of interest.

4.2. Sedimentation Rate (S_r)

The sedimentation rate (S_r) raster dataset was built from the interpolation of the available S_r values for the study area. Data was downloaded from the online database PANGEA (Table 1). The dataset is not ideal, with only 62 samples and poor spatial distribution, likely the main limitation for this study (Figure 5a).

Table 1. Sedimentation rate data and source. *Pangea* website (2014).

Lat dd	Long dd	S_r cm/ky	Lat dd	Long dd	S_r cm/ky	Lat dd	Long dd	S_r cm/ky	Reference
36.69	−11.43	0.389	37.70	−9.47	11.620	37.75	−9.73	20.400	Thiede *et al* [30]
35.35	−10.42	0.969	37.61	−9.28	5.300	37.71	−9.23	7.100	
40.96	−10.72	2.891	37.92	−10.85	7.940	37.70	−9.47	11.620	
36.69	−11.43	0.389	37.72	−10.55	12.040	37.61	−9.28	5.300	
35.35	−10.42	0.969	37.70	−9.77	19.000	37.92	−10.85	7.940	
40.96	−10.72	4.167	37.65	−9.53	7.550	37.72	−10.55	12.040	
37.65	−9.53	7.550	37.68	−10.08	16.180	37.70	−9.77	19.000	
37.75	−9.73	20.400	37.71	−9.23	7.100	34.80	−10.25	2.900	
37.77	−10.18	16.000	37.68	−10.08	16.180	-	-	-	Broecker *et al.* [31]
40.58	−9.86	35.600	37.77	−10.18	33.150	-	-	-	Thomson *et al.* [32]
34.89	−7.82	4.864	34.91	−7.58	4.896	34.86	−8.13	3.210	Sarnthein, Michael (2006) [33]
39.04	−10.66	5.917	-	-	-	-	-	-	Voelker *et al.* [34]
38.63	−9.51	0.001	38.63	−9.51	0.001	-	-	-	Alt-Epping, Ulrich [35]
41.23	−9.07	0.240	41.84	−8.99	0.070	41.21	−9.04	0.350	Recent sedimentation and sedimentary budgets on the western Iberian shelf
41.81	−9.08	0.170	41.17	−9.03	0.420	41.24	−9.03	0.410	
41.84	−9.11	0.200	41.20	−9.04	0.300	41.32	−9.00	0.170	
41.78	−9.07	0.230	41.85	−9.07	0.140	-	-	-	

4.3. Particulate Organic Carbon (P_c)

Particulate Organic Carbon (P_c) depends on the total organic carbon flux to the sea floor [19] and the re-mineralization process on the top centimeters of the sediment column [36–38].

The particulate organic content (P_c) raster applied in this study resulted from kriging interpolation of particulate organic concentration values obtained from the PANGEA online database [39] and core samples analysis U1385 and U1391 from the IODP Expedition 339. Figure 5b depicts the resulting raster file, with larger values of P_c of 2.94 wt. % obtained in the Nazaré’s canyon area, and smaller values in the South Portugal’s EEZ limit area. Again, the limited number of a data points its poor spatial distribution is an important especially in areas distant from the coast. Remineralization processes were not taken into account.

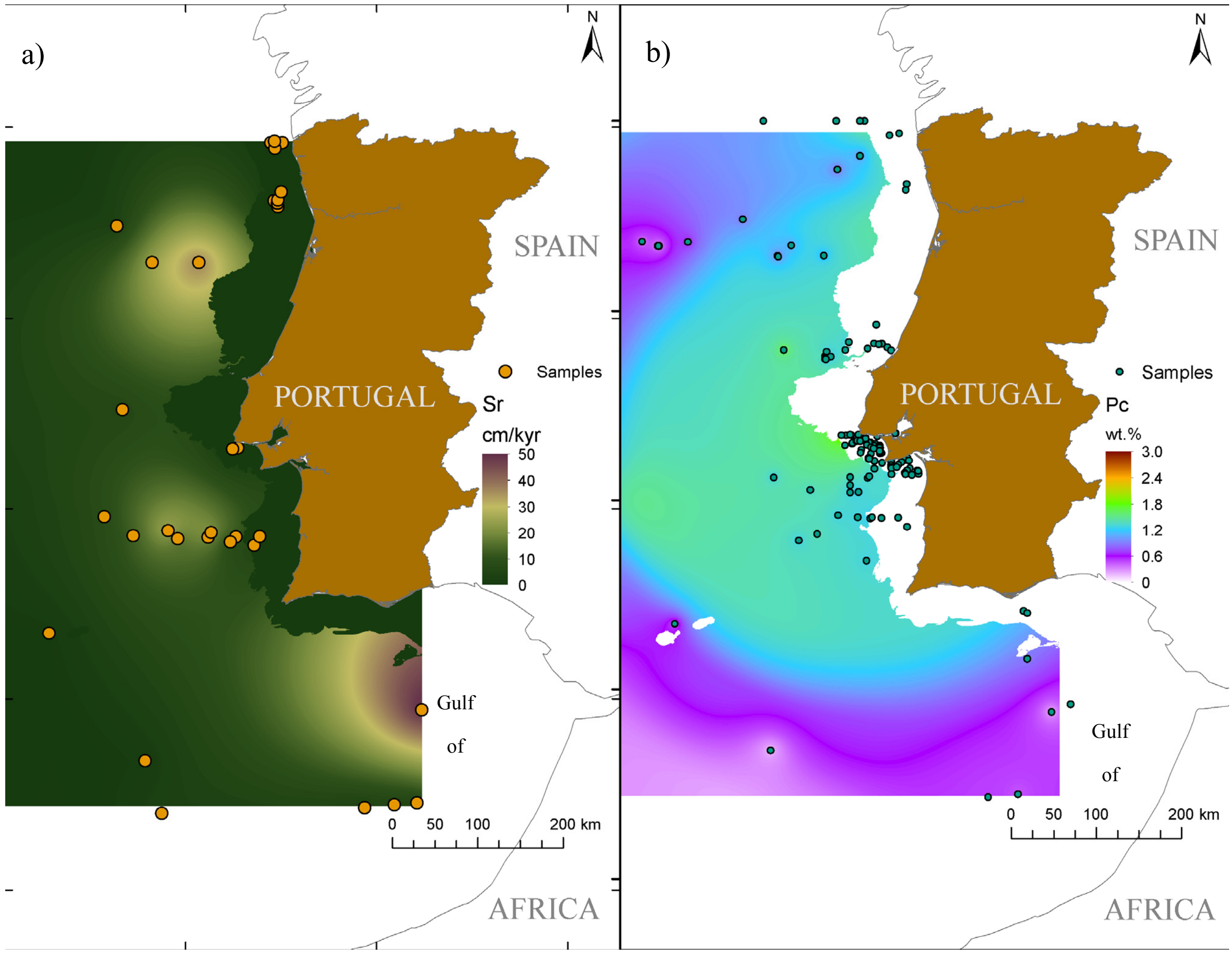

Figure 5. (**a**) Sedimentation rate raster dataset map; (**b**) Particulate Organic Carbon.

4.4. Gas Hydrates Inventory (GHI)

The gas hydrate stability zone defines the area where P and T conditions are sufficient for gas hydrates to be stable, but according to Piñero *et al.* [19] model, the gas hydrates inventory (GHI) is also a function of the organic content and sedimentation rate. GHI was computed for the Full Compaction scenario (Equations (1)) and the Fluid Flow scenarios (Equations (2) and (3)) and sensitivity analysis was conducted varying by 10% each of the variables in Equations (1) to (3).

4.4.1. Full Compaction Scenario

The full compaction scenario retrieved three areas where the formation of biogenic gas hydrates is possible, given the combination of organic matter content and sedimentation rates (Figure 6). The largest area occurs just offshore at some 70 km West-North-West from the coast. Water depths varies in this region from 700 m to 3000 m. A smaller area occurs offshore from the Sines region, in the Tagus abyssal plain, at some 100 km from the coast. Water column varies from 2100 m to 3500 m in this region. The third area occurs just south from the Algarve, at 50 km from the coast and with maximum water depth of 2600 m.

The maximum value estimated for the GHI in the full compaction scenario is 154 kg/m^2, and taking into account the area and concentration variation, the estimated mass is about 493 MtC.

The estimation of the GHI using the full compaction scenario without vertical fluid flow, rises 17% from the original value when S_r is increased by 10% by initial value, while a 10% increase in the P_c value induces a 25% increase in the amount of the GHI, regarding to the maximum of 154 kg/m^2 (Table 2). For the Full Compaction scenario, an average value of 493 MtC of hydrates increases to 840 Mton for a 10% increase in S_r and of 770 MtC for a 10% increase in P_c. In any case the change in the size of the areas where hydrates can form is small indicating that, despite the uncertainty in the S_r and P_c values, gas hydrates are not likely to be formed in areas other than those depicted in Figure 6.

Table 2. GHI estimates for the several scenarios and sensitivity analysis.

	Vertical Fluid Flow with Full Compaction Scenario (cm·yr^{-1})					
	Parameter Variation	***q* = 0.005**	***q* = 0.01**	***q* = 0.015**	***q* = 0.02**	**Parameter Variation**
Average GHI (kg·m^{-2})		22.13	72.69	147.65	282.27	
	22.11	22.13	75.7	151.11	286.55	$\boldsymbol{P_c}$ **10%** wt.%
		22.13	68.08	137.5	262.19	$\boldsymbol{S_r}$ **10%** (cm·kyr^{-1})
Average	493.04	493.04	3590.87	7293.92	13947.23	
GHI	840.49	493.02	3739.71	7465.06	14158.53	$\boldsymbol{P_c}$ **10%** wt.%
(MtC)	769.62	493.04	3362.88	6792.66	12954.94	$\boldsymbol{S_r}$ **10%** (cm·kyr^{-1})

4.4.2. Vertical Fluid Flow and Full Compaction Scenario

The geochemistry of the gas hydrates sampled in the Gulf of Cadiz mud volcanoes indicates a thermogenic origin, and it has been considered that the organic content is too low to allow the formation of gas hydrates with biogenic origin [11]. This is in agreement with the results of our simulations with the Full Compaction scenario (Figure 6a). Nevertheless, Leon *et al.* [23] do not discard the possibility that, in the deeper mud volcanoes, part of the gas hydrates may have a biogenic origin. The vertical fluid flow scenario was included in our analysis to understand if Pinero *et al.* [19] model with full compaction and vertical fluid flow could explain gas hydrates observed in the deeper mud volcanoes. Vertical fluid flow was considered only in the accretionary wedge, where the mud volcanoes are also known to occur (Figure 1).

Given the absence of information about the flow rate in the area, values of q = 0.005 cm/yr; q = 0.01 cm/yr; q = 0.015 cm/a and q = 0.02 cm/yr were considered. Notice that these values of q were considered over the entire area of the accretionary wedge. This is a simplifying assumption, not only because fluid flow is dependent on the petrophysical properties of sediments, but mainly because it is well known that in the Gulf of Cadiz, vertical fluid flow is associated to tectonic features and mud volcanoes. However, these linear features are nor amenable to be analyzed with a large-scale GIS as applied in this study, and thus fluid flow was distributed uniformly in all the accretionary wedge.

Figure 6b shows the results for the q = 0.01 cm/yr scenario. According to the vertical fluid flow model, biogenic gas hydrates can form in the accretionary wedge zone. Even for the lowest flow rate (q = 0.005 cm/yr), gas hydrates can form in the accretionary wedge zone. Simulations with other values of q indicate that GHI estimation rises with the fluid flow value (Table 2). Thus, Piñero *et al.* [19]

model with vertical fluid flow is consistent with Leon *et al.* [23] possibility that some of the hydrates observed in the mud volcanoes may be from biogenic origin, since the organic carbon and sedimentation rate appears to be sufficient as long as vertical fluid flow is considered.

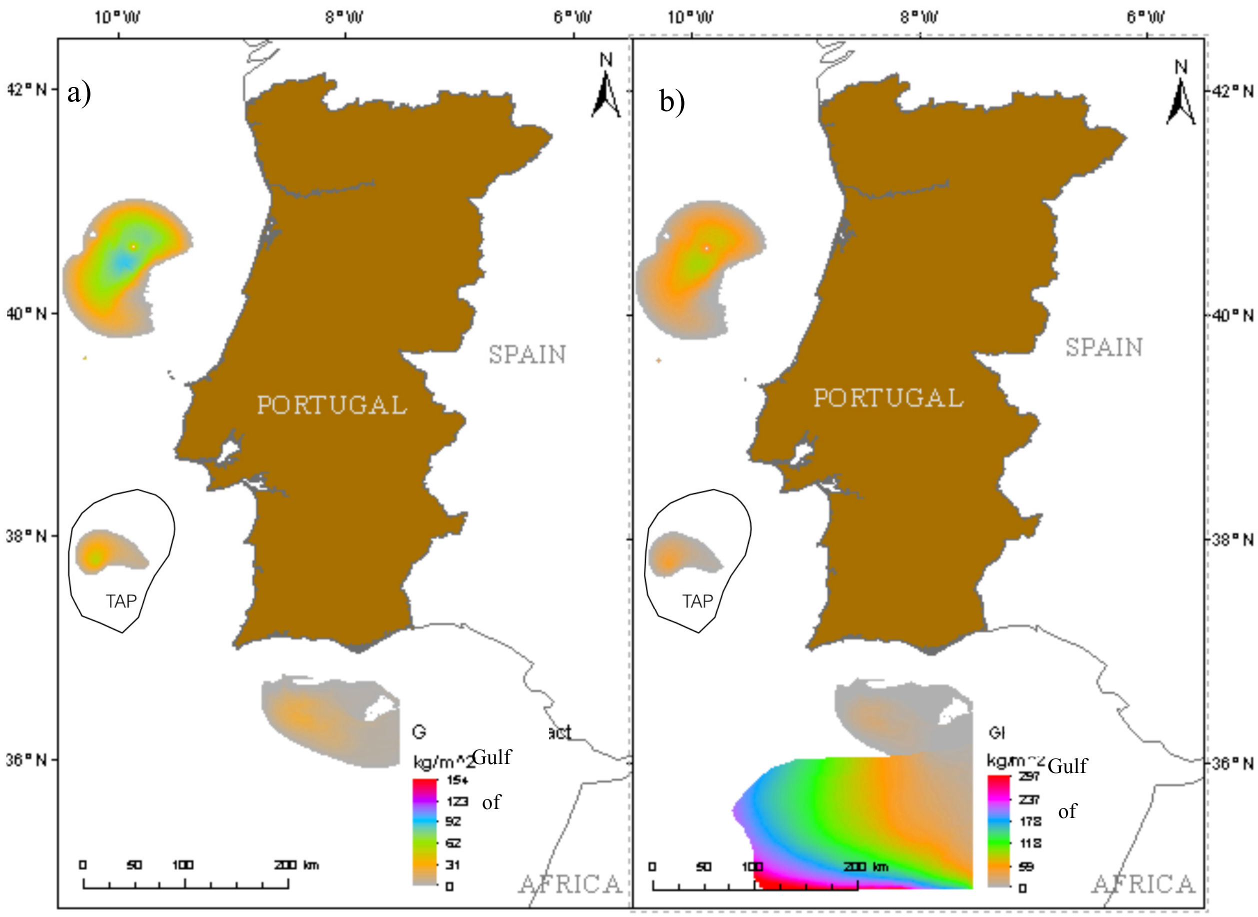

Figure 6. (**a**) GHI in the Full Compaction scenario; (**b**) GHI in the Full Compaction with fluid flow in the accretionary wedge (q = 0.01 cm/ky).

5. Discussion

Bernardes *et al.* [5] delimited the CO_2 hydrates stability zone in the Portuguese continental margin and applied four criteria to delineate the areas most suitable for CO_2 storage as hydrates, namely: (i) Distance from the main ports; (ii) Water column depth; (iii) thickness of the CO_2 hydrates stability zone; and (iv) Spatial variation of the hydrates stability zone thickness. Three preferential areas were defined as more suitable for CO_2 injection, possibly coupled with recovery of methane, if gas hydrates exist in those same areas.

CO_2 hydrates are stable only at more than 1100 m water depths, while gas hydrates are stable at around 600 m depths. Thus, it is the CO_2 stability that constrains the depths, and consequently the distance from the mainland, at which CO_2 storage coupled with methane recovery could be conducted.

Figure 7 overlaps the areas defined by Bernardes *et al.* [5], with the areas defined in the GHI conducted in this study. Two of the areas partly coincide. In a perspective of potential recovery of methane from gas hydrates and CO_2 storage, future research should focus in those overlapping two areas (Figure 7).

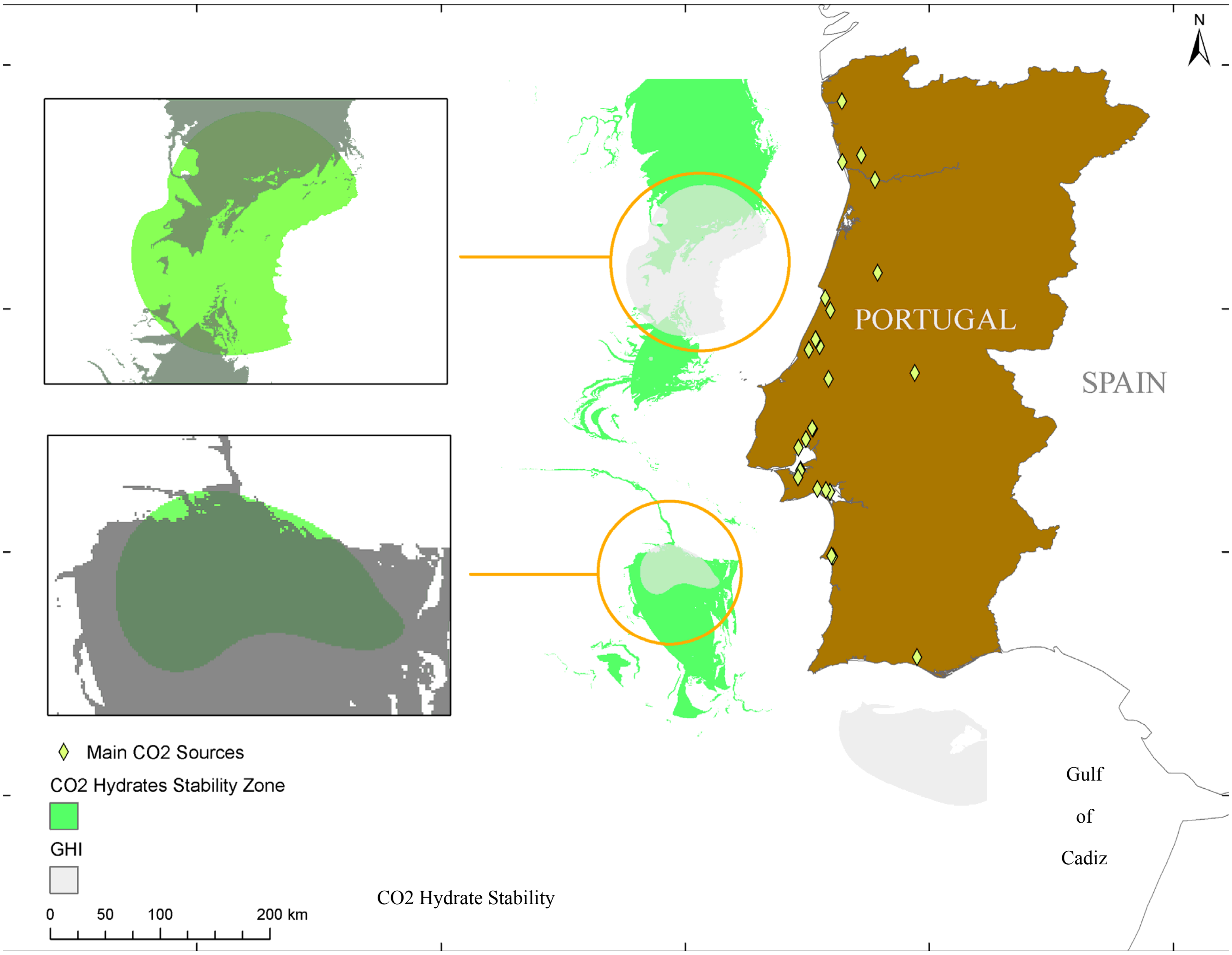

Figure 7. Overlap of preferential areas for CO_2 storage in hydrate form with GHI areas.

6. Conclusions

Countries with a deep continental margin not distant from the shoreline may envisage the reduction of greenhouse gas emissions from the storage of CO_2 as hydrates in sub-seabed sediments. Portugal is one of those countries, where the shallow offshore (bathymetry < 200 m) is, in some areas, less than 10 km wide. However, economic feasibility of that option can only come from added value of recovering CH_4 from existing gas hydrates. Storing CO_2 hydrates with simultaneous recovery of CH_4 from gas hydrates can contribute to mitigate climate change, while addressing the increasing energy demand. The goal of this article was to define areas, in the Portuguese geological continental margin, simultaneously with conditions favorable to the stability of the CO_2 hydrates and gas hydrates.

A GIS was implemented with data on bathymetry, pressure, seabed temperature, sediment thickness, organic carbon content, sedimentation rates and an updated geothermal gradient.

A non-linear approximation to the CSMHYD gas hydrate phase boundary was adjusted and implemented on a Fortran code, *CO2hydrate*, able to perform analytical calculations in the GIS data grid. The code delineates areas where hydrates are stable and computes the thickness of the gas hydrate stability zone (GHSZ).

Gas hydrates are stable at water depths over 600 m, contrasting to the 1100 m water depth required for the CO_2 hydrates stability (Bernardes *et al.*, [5]. The average thickness of the GHSZ is averaged in 528m, with a maximum value of 798 m.

An estimation of the Gas Hydrate Inventory (GHI), resorting to Piñero *et al.* [19] transfer functions, was conducted for a Full Compaction scenario and for the vertical fluid flow scenario in the accretionary wedge, South from Algarve, due to the known occurrence of gas hydrates in connection to mud volcanoes.

The Full Compaction scenario indicates that gas hydrates can form in the Portuguese continental margin in three main areas. Two of those areas coincide with the areas defined by Bernardes *et al.* [5] as suitable for storage of CO_2 in hydrate form. Future research focusing on those areas, should assess existing seismic sections in order to verify the existence of a BSR, and collect accurate data on the particulate organic carbon and the sedimentation rate. Furthermore, and in order to test the possibility of CO_2 injection, petrophysic and hydraulic characterization of the sub-seabed sediments should be conducted.

The simulations including vertical fluid flow indicate that it is possible for biogenic gas hydrates to form in the area of the accretionary wedge, even though the particulate organic carbon is not high. This corroborates Leon *et al.* [23] assertion that, in some of the mud volcanoes, the biogenic origin of part of the gas hydrates should not be discarded.

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Author Contributions

Luís Bernardes had the idea of the work, managed the data, its GIS implementation and paper writing. Júlio Carneiro designed the *CO2Hydrate* computer model. Pedro Madureira was the contacts manager for data access and geological adviser. Filipe Brandão was the GIS adviser. Cristina Roque was the marine geology adviser.

Conflicts of Interest

The authors declare no conflict of interest.

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