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Effectiveness of Oxygen-Saturated Seawater Injections and Air Sparging Technologies in Remediation of Coastal Marine Sediments from Sludge

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Abstract:	The occurrence of hypoxic muddy sediments on shallow beaches and other sheltered areas is a well-known environmental problem, which negatively affects coastal areas, tourism potential, the public use of beaches and sediment biodiversity. The usual solution is limited to dredging and removal of sludge to a landfill site. In this study, a laboratory scale experiment was performed to determine the effectiveness of two technologies: a modification of air sparging and a new approach based on injecting oxygen-saturated seawater in hypoxic muddy sediments (oxygen-saturated seawater injectionsmethod), for remediating sludge in coastal sediments, minimizing environmental impact respect to dredging. Our results showed that both technologies significantly increased dissolved oxygen content in pore water, facilitating the oxidation of more than 90% of the organic matter, and other reduced inorganic compounds such as sulphide, with the consequent increase of sulphate concentration from 0.3 to 3.0 g·L-1. Moreover, a rise of redox potential from -258 mV to above 200 mV, and a dramatic drop in chemical oxygen demand were also indicators that oxic conditions had been restored. After 65 days, soft, black, muddy and hypoxic sediment with high organic matter content and a characteristic fetid odour was transformed into well-oxygenated sediment, which had a low organic matter content and had lost its initial shiny black colour and odour. The main difference between both technologies was the depth influenced by sediment remediation, oxygen-saturated seawater injections affected deeper areas than clean pressurized air injections.
Response to Reviewers:	Reviewer #1: The ms entitled "Effectiveness of Oxygen-Saturated Seawater Injections and Air Sparging Technologies in Remediation of Coastal Marine Sediments from Sludge"

brings the comparison between two techniques for sediments remediation. Although the foundations of both techniques are quite similar, the OSSWI seems to be a promising tool if correctly implemented.
It is somewhat unfortunate, however, that the ms is rather confusing describing the experiments performed, with no well-defined hypothesis, experimental design not enough explained, poorly written results with English needing a thorough review, particularly the grammatical tense coherence along the ms.

-The manuscript has been thoroughly revised to improve all aspects indicated by reviewer #1. Please, check the changes made to the manuscript.

The introduction opens expectations not fulfilled in the following sections. It is written focused on sediments remediation in beaches for recreation activities, but only a lab experiment has been performed. The statement in line 112 that "the goal of this study was to compare the effectiveness of both technologies to improve the physicochemical properties of coastal sediments and to enhance conditions for recreational use of shallow beaches" is not in accordance with the experiment performed not even at pilot scale in the field. Did the authors perform a larger experiment in the field? What would be the infrastructure needed to scale the obtained results? Would that be doable to larger scales?

-The introduction and aims of the study have been modified to be consistent with the laboratory-scale research that has been performed. Please, see the manuscript

The schematic sketch of the system in Fig 1 needs to be completed with a photograph of the system in order to provide a clear and precise idea of what and how the experiment was performed.

-The schematic drawing of the experimental setting (Fig 1) has been completed and pictures of the experimental system has been included in the supporting information section.

Lines 127 to 131 needs be rephrased to better and clearly understand the procedure. It is stated that experimental conditions were simulating natural conditions but no measurements of any natural condition is reported.

-The sentences in lines 127 to 131 have been rewritten and information about the natural sea conditions at Marineta Casiana beach have been included. Please, see the manuscript.

Experimental design must be clearly stated from the beginning, only at the end of the section the reader realize that 4 cores were used for AS, another 4 for OSSWI and another 4 for control.

The distribution of the cores according to the applied treatment has been included at the beginning of materials and methods section. Please, see the manuscript.

No reference of control results is made along the ms.

-The aim of the study was to compare the efficacy of the two techniques (AS and OSSWI) for remediating sludge in coastal sediments. The control was only used to confirm that the parameters studied (temperature, salinity, pH, DO content, COD, sulphate concentration, %OM and redox potential) remained constant in the untreated samples throughout the trial, i.e., with similar values to those determined at initial sampling time (time 0)).
The control was not included in the factorial analysis of variance. For the fixed factor Treatment, only AS and OSSWI were considered. Please, see the manuscript.
For all these reasons, the control is not cited in results and discussion sections.

It is not clear whether water was directly pumped from the sea to the container every 15 days and then used in the system or directly pumped to the whole system. It would be much useful to add a picture of the pipe and mesh tube to Fig 1 (Line 147)

	-The water was directly pumped from the sea to the container every 15 days and then, used in the system. The sentence has been rewritten. Please, see the manuscript. Line 181 - delete second time "treatment" -The change has been made in the manuscript. Please, see ms Line 183 - is %DO the percentage of saturation or mg/L? state clearly. -In the manuscript, DO content has been expressed as mg/L. The manuscript has been revised and the units of DO concentration have been unified. Please, see the manuscript. Meaning of letter in Figures 2 to 5 is not clear and need further explanation, neither explanation given in figures caption. -The explanation in the figures caption has been included. Please, see the manuscript Reviewer #2: Authors have presented a good article related to the possibilities of solving a real problem in many areas, but specially un touristic areas like these, in the Mediterranean sea. The importance of this article is more than that related to recover recreational areas. I think that this can be also applied to recover natural areas affected by wastes that can produce hypoxic muddy sediments. Although it is a lab experiment, the results are promising and can be useful to proceed to design an experiment in the site. However, this process needs later an economic feasibility study. The article is, in my opinion, well written and organized, and materials and methods, results and discussion are adequate and length satisfactory. The problem of this type of hypoxic muddy sediments in touristic areas is great because of the rejection produced to the visitors. Please check the following possible mistakes: Page 4, line 90. The reference given is "European Comission 2000", please confirm if this reference is the same given in REFERENCES "European Waste catalogue 2000" or is a missed reference. -It was an error, and the reference has been changed. Page 11, lines 322, 324 and 325, the units of the data given are cut by the end of the line. I know this not a mistake but some attention should be given during editing process. -Thank you for your appreciation, we will pay attention to the details so that this error does not occur.

Effectiveness of Oxygen-Saturated Seawater Injections and Air Sparging Technologies in Remediation of Coastal Marine Sediments from Sludge

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Abstract

The occurrence of hypoxic muddy sediments on shallow beaches and other sheltered areas is a well-known environmental problem, which negatively affects coastal areas, tourism potential, the public use of beaches and sediment biodiversity. The usual solution is limited to dredging and removal of sludge to a landfill site. In this study, a laboratory scale experiment was performed to determine the effectiveness of two technologies: a modification of air sparging and a new approach based on injecting oxygen-saturated seawater in hypoxic muddy sediments (oxygen-saturated seawater injections method), for remediating sludge in coastal sediments, minimizing environmental impact respect to dredging. Our results showed that both technologies significantly increased dissolved oxygen content in pore water, facilitating the oxidation of more than 90% of the organic matter, and other reduced inorganic compounds such as sulphide, with the consequent increase of sulphate concentration from 0.3 to 3.0 $g \cdot L^{-1}$. Moreover, a rise of redox potential from -258 mV to above 200 mV, and a dramatic drop in chemical oxygen demand were also indicators that oxic conditions had been restored. After 65 days, soft, black, muddy and hypoxic sediment with high organic matter content and a characteristic fetid odour was transformed into well-oxygenated sediment, which had a low organic matter content and had lost its initial shiny black colour and odour. The main difference between both technologies was the depth influenced by sediment remediation, oxygen-saturated seawater injections affected deeper areas than clean pressurized air injections.

Keywords: Muddy sediment; Hypoxia; Organic matter; Oxidation; Shallow beach; Remediation.

1. Introduction

Hypoxia has become a world-wide phenomenon in the coastal areas, with serious consequences for marine ecosystems such as fish death and mortality of benthic species (Zhang et al. 2010). The incidence and extent of coastal hypoxia has risen over the last century, due to the impact of both natural and anthropogenic stresses (Diaz and Rosenberg 2008). There are many factors governing hypoxia and identifying the specific causes is difficult due to the interacting processes in the coastal zone (Caballero-Alfonso et al. 2015).

On the Mediterranean coast, hypoxic sediments are often found on beaches heavily sheltered by ports or breakwaters, where low hydrodynamism promotes fine material sedimentation as well as organic matter (OM) deposits, leading to the appearance of reducing conditions (Montefalcone et al. 2007). In addition to the problem of anaerobiosis caused by anthropogenic factors, changes in benthic marine communities have occurred during the last few decades, where the alga *Caulerpa prolifera* has partially replaced the seagrasses *Posidonia oceanica* and *Cymodocea nodosa* (Meinesz et al. 2001; Lloret et al. 2005; Pérez-Ruzafa et al. 2012). In areas of extensive algae growth, *C. prolifera* further increases the deposition of fine particles, due to the shape of its blades, and has increased OM inputs as a result of the high amount of biomass that it generates (Hendriks et al. 2010; Pérez-Ruzafa et al. 2012). Studies by Han and Liu (2014) have demonstrated that the rapid growth of *C. prolifera* meadows significantly reduces the passage of the light limiting photosynthesis by seagrasses growing in the same area. This limits the replenishment of the oxygen consumed and leads to a progressive oxygen depletion in areas colonized by this alga (Han and Liu 2014). These conditions trigger a sharp reduction in the sediment of sulphate to hydrogen sulphide (H_2S), a highly toxic compound for benthic organisms and seagrasses (Terrados et al. 1999; Middelburg and Levin 2009). A high concentration of H_2S combined with the presence of ferrous ions (Fe^{2+}) in these environments promote the formation of amorphous ferrous sulphide (FeS), which are highly insoluble. Ferrous sulphide and the large amount of OM accumulated in these sediments impart a shiny black colour and foul odour to the sediments (Asaoka et al. 2009; Duarte et al. 2015). When this sludge builds up close to the shoreline, it seriously affects the environmental quality of the beach and decreases its potential for tourism and public use (Boese et al. 2000).

To date, dredging has been the most frequently employed method for remediating sludge on Mediterranean beaches. Under European legislation, once these sediments have been removed from their natural environment, they are considered waste and should be treated in accordance with the current regulations (European Commission 2020). In practice, this generally entails dumping in landfills, which is an environmentally unsafe solution. It is therefore necessary find new sediment remediation methods which have less of an environmental impact.

Currently, Air Sparging (AS) has become one of the most implemented *in situ* removal technologies because of its high efficiency, speed and low economic cost (Adams and Reddy 2000; Bass et al. 2000; Kim et al. 2015; Song et al. 2015). Moreover, site remediation could be performed without excavation, minimizing the environmental impact in respect to dredging (Tsai 2007). AS is a process by which clean pressurized air is introduced directly into the saturated zone to induce volatilization of volatile organic compounds (VOCs) (Rogers and Ong 2000; Waduge et al. 2004; Yao et al. 2017). Commonly, the volatilized organic compounds are transferred to the atmosphere from the saturated zone by the flow of air or by some type of vapour extraction system (Peterson et al. 2000). In addition to the air stripping process, AS also promotes biodegradation of pollutants by increasing oxygen concentration into the saturate zone, stimulating aerobic degradation of these substances (Mortensen et al. 2000; Ghabayen et al. 2013). In general, AS is applicable at sites where groundwater or saturated soils are contaminated with volatile and semivolatile organic pollutants such as petroleum hydrocarbons, mineral oils, or halogenated substances. However, these pollutants are rarely present in the coastal areas under study (shallow beaches), where the hypoxic muddy sediment is formed by the increase of OM inputs (alga and seagrass remains) (Boese et al. 2000). For this reason, there are no studies that demonstrate the efficacy of AS under these conditions.

Dissolved oxygen content in pore water has been shown to be the dominant rate-limiting step in the natural degradation of organic matter deposits in coastal muddy sediments (Duarte et al. 2015). Therefore, injections of aerated water into these sediments could be useful in transporting oxygen near solid deposits, resulting in the oxidation of organic matter and ferrous sulphide accumulated (Duarte et al. 2015). Based on these facts, we proposed a new methodology involves injecting oxygen-saturated seawater to displace hypoxic pore water in the sediments and thus, restore good oxidizing conditions (Ferrández et al. 2017).

The goal of this study was to compare the effectiveness of both modified Air Sparging (AS) and Oxygen-Saturated Seawater Injections (OSSWI) technologies to improve the physicochemical properties of coastal hypoxic muddy sediments, under controlled laboratory situations.

2. Materials and methods

2.1. Sampling and experimental settings

The study was carried out at laboratory-scale using sediment samples collected randomly from a 200 m^2 area located 25 m from the shore on Marineta Casiana beach in the south of Dénia port (Alicante, Spain) (38º 51′ 17,837” N 00º 05′ 14,192” E). Without altering the soil vertical profile, the extracted sediment was introduced into nine cylindrical columns of polyvinyl chloride (PVC), 60 cm of high and 16 cm of internal diameter, until reaching a height of 40 cm inside the cylinders. In order to ensure that the samples remained saturated, sufficient seawater was added to the top of the columns to cover the sediment surface, and then, the columns were sealed with polyoxymethylene caps and nitrile rings.

Once in the laboratory, the nine columns containing the sampled sediment (4 for AS treatment, 4 for OSSWI treatment and 1 for Control) were uncovered and deposited in a PVC container holding 120 L of seawater. The seawater in the container was renewed every 15 days to avoid salt concentration due to water loss by evaporation. The water was drained through a drainage hole, connected to a suction pump (Fig. 1) and the container filled again with water directly pumped from the sea.

The container was fitted with two aeration pumps to prevent water stagnation, and a water recirculation system was mounted on the columns using water from the container to simulate marine conditions of Marineta Casiana beach (average surge period: 4.8 s and average surge height: 0.31m) (Puertos del Estado 2021) (Fig. 1). This ensured that the samples received a constant flow of seawater until the column overflowed, at an exchange rate of 0.5 $mm \cdot day^{-1}$ (Fig. 1), the mean water column exchange rate in the sampling area. A temperature of 20 ºC was maintained throughout the experiments.

The oxygen-saturated seawater injections treatment (OSSWI treatment) was applied to 4 of the 9 sediment samples. These samples were injected with oxygen-saturated seawater (6.5 mg dissolved $oxygen \cdot L^{-1}$ to 25 ºC, 1 atm), pumped with a pump Eheim® 230 V, through a hydraulic circuit mounted on the columns, consisting of non-transparent pipes of 16 mm in diameter (Fig. 1). To obtain the oxygen-saturated seawater, a suction pump was used to collect it from the sea and fill a 25 L container, which was then connected to a continuous air-bubbling system. A 0.2 kW blower fitted with fine bubble diffusers (5 µm) ensured a constant bubbling until reaching a dissolved oxygen concentration higher than 80% of saturation. The oxygen-saturated water was injected to a depth of 20 cm (Fig. 1). Injection was performed using a non-transparent pipe of 6 mm in diameter and sealed at the end, containing 18 perforations measuring 1 mm in diameter and distributed evenly in a 1 cm section located 3 cm from the sealed end (Fig. 1). The aim of the perforations was to achieve spherical diffusion into the marine sediment.

Modified air sparging technology was applied to 4 of the 9 sediment samples. AS was simulated by introducing pressurized air through a vertical sparge well, which consisted of a 6 mm diameter PVC pipe sealed in the end. The lower 3 cm of the pipe were perforated with 1 mm diameter holes, which were warped with stainless-steel mesh. The vertical sparge well was installed at the centre of sediment column (Fig. 1). The air injections were performed at 20 cm below the sediment surface just like oxygen-saturated water injections (Fig. 1). The pressure (300 kPa) and flow rate (1.5 $L \cdot min^{-1}$) were adjusted until a radius of influence of 20 cm was reached.

Both oxygen-saturated seawater and air injections were performed for 65 days with an injection frequency of 180:60 min (resting:injection).

One column containing a sediment sample remained untreated (Control treatment). The Control was used to confirm that the parameters studied (temperature, salinity, pH, dissolved oxygen concentration, chemical oxygen demand, sulphate concentration, percentage of organic matter and redox potential) remained constant throughout the experiment, with similar values to those determined at initial sampling time (time 0).

2.2. Pore seawater analysis

Pore seawater samples were collected at 0 (initial and just after sampling), 10, 25, 45 and 65 days after the initial OSSWI or AS treatments and at 10, 20 and 30 cm from the top of the sediment by a stainless-steel tube (ø: 6 mm, h: 50 cm), provided with a stainless-steel mesh on the bottom and attached to a 50 mL syringe. Salinity, pH, temperature, dissolved oxygen (DO), chemical oxygen demand (COD) and sulphate concentration were measured. Salinity (expressed as CE), pH, temperature and DO were directly determined by a conductimeter (Crison EC-Metro GLP 31®), a pHmeter (Crison Micro-pH2000®), a thermometer and an oximeter (Crison Oxi 45®) respectively. The pore water samples for COD and sulphate analysis were filtered through 0.45 µm membrane filters (Simplepure® PTFE/L). Thereafter, the concentration of sulphate was determined by Ion Chromatography (IC) with conductivity detector, according to the standard method (Rice et al. 2017). The column used was a Metrosep A 7-250 Metrohm®, 250 mm x 4 mm, with a flow rate of 0.8 $mL \cdot min^{-1}$, an oven temperature 40 ºC, and injection volume 20 µL.

The mobile phase consisted of Na_2CO_3 3.6 mM. COD was determined by the dichromate method (Baumann 1974).

2.3. Sediment analysis

Samples for sediment analysis were collected 0 (initial), 10, 25, 45 and 65 days after the oxygen-saturated seawater or clean pressurized air injections. Sediment temperature was measured with different temperature sensors located in the containers at 10, 20 and 30 cm of depth. Sediment was sampled at 10 and 20 cm from the top using a steel tube (ø: 30 mm, h: 30 cm). Redox potential (E) was measured immediately using an electrode (InLab®). Thereafter, %OM was determined in the sediment samples in accordance with Walkley-Black methodology (Leong and Tanner 1999).

2.4. Statistical analysis

Results obtained were statistically evaluated with factorial analysis of variance with the SPSS software (23.0 version), using treatment (AS or OSSWI) (T), depth (cm from the top of sediment) (D) and treatment period (in days) (P) as fixed factors. In this analysis, both the effect of each factor on the variables analyzed (Temperature, salinity, pH, DO content, COD, sulphate concentration, %OM and redox potential), and the possible interaction between factors were analyzed. Statistically different groups were determined using Duncan's test ($p<5\%$).

3. Results

3.1. Pore seawater

ANOVA p-values for the three fixed factors (Treatment [T], Depth [D] and Time Period [P]) and the double and triple interactions between these factors (TxD, TxP, DxP and TxDxP) are shown in Table 1. As it can be observed, neither the temperature nor the salinity of the pore water were affected by the three factors or their interactions (Table 1), indicating that these parameters did not undergo significant changes over the course of the experiment.

3.1.1. pH

The fixed factors [D] and [P] significantly affected the pH value obtained for the pore water, as well as TxP interaction (Table 1). However, neither the treatment with OSSWI or AS ([T]), nor none of the other double and triple interactions of the three fixed factors significantly affected the pH value of pore water (Table 1).

Pore water pH in OSSWI-treated samples fell from an initial value of 7.60 to 7.06 after 25 days of treatment (Fig. 2A). After that, pH values slowly rose again, reaching a final value of 7.48 by the end of the experiment (Fig. 2A). Although pH values in the AS-treated samples showed a similar trend to that observed in OSSWI-treated samples during the first 25 days of treatment (Fig. 2A), significant differences in the pH behaviour were found for the last two samplings (Fig. 2A). Pore water pH of OSSWI-treated samples increased 5.6% in the last two samplings, while pH of AS-treated samples increased 2.6% in the same period of time (Fig. 2A).

In relation to the effect of depth, our results indicated that the pore water at 20 cm depth showed a slightly lower pH value (pH 7.26) than that observed at 10 and 30 cm (pH 7.44 and 7.42, respectively), with no significant differences being detected between these latter two depths (Fig. 2B). This indicated that a central zone formed in the sediment, which coincided with the point of injection of oxygen-saturated seawater or clean pressurized air, presented a slightly lower pH than that of the zones above and below the injection point. The differences in pH between these zones were small (≈0.2 pH units), albeit statistically significant (Fig. 2B).

3.1.2. Dissolved oxygen concentration

Table 1 shows that the three fixed factors ([T], [D], and [P]), and the all double interaction between them (TxD, TxP, DxP). These factors significantly affected DO content in the pore water, whereas the triple interaction (TxDxP) did not have a significant effect on this parameter (Table 1).

As can be seen in Fig. 3A, DO concentration in pore water increased over the first 45 days of OSSWI treatment, from an initial condition of hypoxia (1.67 mg DO·L^{-1}) to a DO concentration capable of supporting most of the aquatic organisms in the area (5.86 mg DO·L^{-1}, (Bain 1999)) (Fig. 3). Statistically significant differences in DO content between the last two samplings (45 and 65 days of the experiment) were not found (Duncan`s test) (Fig. 3), indicating that DO concentration had remained constant over the last 45 days of treatment.

The AS-treated samples performance was statistically similar to the OSSWI-treated samples through the first three sampling (Fig. 3), since pore water DO concentration rose from initial value of 1.67 mg DO·L^{-1} to 4.6±0.2 mg DO·L^{-1} for AS-treated samples and 4.8±0.2 mg DO·L^{-1} for OSSWI-treated samples, after 25 days of treatment. In contrast, DO concentration in pore water of AS-treated samples was statistically lower than that in OSSWI-treated samples from the third sampling. (Fig. 3A). This statistically significant difference in the DO concentration between the both treatments remained until the end of the study, with a significant lower level of oxygen in the pore water of AS-treated samples respect to OSSWI-treated samples (Fig. 3A).

The variation of the average DO content in AS and OSSWI treated pore water at the three depths studied is represented in Fig. 3B. No statistically significant differences were found in DO content between AS and OSSWI treatments for injection zone (20 cm depth) nor for 10 cm depth from the top of sediment (Fig. 3B). However, at 30 cm depth, the OSSWI treatment increased the dissolved oxygen concentration compared to AS treatment. Specifically, the sediment treated with OSSWI showed a concentration of dissolved oxygen 6% higher than that treated with AS (Fig. 3B) at this depth.

3.1.3. Chemical oxygen demand

The factors [D] and [P] and the interaction (TxD) had a statistically significant effect on COD in the pore water (Table 1). In contrast, [T] and TxP, DxP and TxDxP interactions did not significantly affect this parameter (Table 1).

COD values fell steadily over time in both AS and OSSWI-treated samples alike (Fig. 4A). As with the DO content, statistically differences in COD values between AS and OSSWI-treated samples were just found at a depth of 30 cm, with the lower reduction of COD in the pore water of samples treated with clean air pressurized injections (Fig. 4B). In this way, the decrease of COD value at a depth of 30 cm was a 10% greater in OSSWI-treated samples than in AS-treated samples (Fig. 4B). However, there were not significant differences between both treatments at the upper layers, 10 and 20 cm, respectively (Fig. 4B).

3.1.4. Sulphate concentration

The ANOVA p-values shown in Table 1 indicate that the three fixed factors ([T], [D] and [P]) and TxD y TxP double interactions had a significant effect on the concentration of sulphate in the pore water, whereas DxP and triple interaction of the fixed factors (TxDxP) did not significantly affect the concentration of this anion (Table 1).

The concentration of sulphate in the pore water remained constant over the first 10 days of OSSWI treatment and over the first 25 days of AS treatment, and then rose from an initial concentration of 0.29

$g \cdot L^{-1}$ to 2.61 $g \cdot L^{-1}$ for OSSWI treatment and to 2.40 $g \cdot L^{-1}$ for AS treatment, after 65 days of experiment (Fig. 5A). These results indicate that after 65 days of treatment, oxygen-saturated water injections allowed to achieve a sulphate concentration in the pore water statistically higher than that achieved with clean pressurized air injections (Fig. 5A).

The average sulphate concentration at the injection site (20 cm deep) and at 10 cm depth was statistically the same for both treatments (Fig. 5B). However, at 30 cm depth, the sulphate concentration in the OSSWI-treated sediment was 13% higher than in the AS-treated sediment (Fig. 5B).

3.2. Sediment

3.2.1. Percentage of organic matter

According to the ANOVA p-values given in Table 1, only [D] and [P] factors and DxP interaction had a significant effect on the content of OM in the sediment. While double, and the triple interactions of factors did not affect this parameter.

OM content in the sediment decreased along time for the two depths analyzed (10 and 20 cm) (Fig. 6). The initial OM content at 20 cm (6.81 ±0.07) was 24% higher than at 10 cm (4.19±0.05) (Fig. 6), which is why the former depth was selected as the point of injection. However, once OSSWI or AS treatment were applied, the percentage of OM at 20 cm became statistically equal to that observed at 10 cm in depth throughout the experiment (Fig. 6). This result suggests that OM was initially degraded more rapidly at the point of injection than elsewhere; thus, 73% of the OM present at 20 cm depth had been oxidized after 10 days of treatment, compared with the 59% at 10 cm (Fig. 6).

It should be noted that no significant differences in the degradation process of OM were found between OSSWI and AS treatments (Table 1). This is in agreement with DO, CDO and sulphate concentration results since up to the first 20 cm the response of both OSSWI and AS treatments was the same (Figs. 3B, 4B and 5B). Moreover, although both OSSWI and AS treatments were maintained for 65 days, only 45 days were required to reduce sediment organic load by around 90% (Fig. 6).

3.2.2. Redox potential

Unlike the other parameters analyzed, only two variables were studied for redox potential: Treatment [T] and Time Period [P], because potential was only measured using a redox electrode at 20 cm depth. Only [P] fixed factor and TxP interaction significantly affected sediment redox potential (Table 1).

As it can be seen in Fig. 8, oxygen-saturated seawater injection or clean pressurized air injection increased sediment redox potential from an initial condition of hypoxia (-257 mV) to good oxygenation conditions (>200 mV) after 65 days (Fig. 7). Although, the increase in redox potential in the OSSWI-treated sediment was faster during the first 10 days of treatment than in the AS-treated sediment (Fig. 7).

4. Discussion

Our results revealed a clear trend towards a reduction in pore water pH in AS and OSSWI-treated samples alike (Fig. 2A). According to Asaoka et al. (2009), this reduction in pH may be associated with the release of organic acids produced during the decomposition of OM in the sediment. However, Spiro and Stigliani (2004) and Hargrave et al. (2008) have suggested that processes such as sulphide oxidation to sulphate and/or the respiration of microorganisms in the medium also may contribute to lowering the pH. Iron (II) oxidation and the subsequent iron hydroxide formation through the reaction: $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$, undoubtedly contributes to pH lowering. A comparison of the pH and OM evolution (Figs. 2A and Fig. 6) revealed a good correlation between them, whereby a reduction in pH was accompanied by a reduction in sediment organic load. The lowest pH values were measured at the injection point (Fig. 2B), which coincides with the point of higher OM oxidation after 10 days (73%), compared to the 49% at 10 cm (Fig. 6).

Pore water pH increased after 25 days of AS and OSSWI treatments, which may have been due to the lower intensity of the redox reactions and the buffer effect of carbonates present in the sediment, which was of limestone origin (Asaoka et al. 2009). Thus, if the flow of protons generated by OM and metal oxidation fell, pore water pH would return to initial values (Asaoka et al. 2009). After only 25 days of AS or OSSWI treatments, ≈80% of the OM had been degraded (Fig. 6); therefore, the subsequent flow of protons would have been insufficient to counteract the buffer effect of the carbonates, explaining the observed rise in pH. (Fig. 2A).

According to Hargrave et al. (2008), the redox potential of a medium must fall within the range 0 to 200 mV because the spontaneous oxidation of sulphide to sulphate. The sediment redox potential at the beginning of the assay was around -257 mV, and therefore the reaction that was taking place was the reduction of sulphate to sulphide, explaining the foul odour of the sediment, due to the detachment of H_2S and the formation of FeS. However, after 10 days of OSSWI treatment or 25 days of AS treatment, the redox potential had risen above 0 mV, which would explain the subsequent increase in the concentration of sulphate in the medium (Fig. 5A). Our results showed that after 65 days of both OSSWI and AS treatments, pore water sulphate concentration was in the expected range for good quality seawater (≈3 $g \cdot L^{-1}$) (Webber and Thurman 1991).

As for the dissolved oxygen concentration in the sediment, the initial hypoxia situation (<2 mg $DO \cdot L^{-1}$) changed to an acceptable DO content capable of supporting an unaltered infaunal community (≈5.7 mg $DO \cdot L^{-1}$, (Bain 1999)) after 65 days of both OSSWI and AS treatments. However, at no time did it reach >6.5 mg $DO \cdot L^{-1}$ to 25ºC, the minimum value required to be classified as good quality water (Appel *et al.* 2006). Oxidation of OM (Fig. 6) and subsequent sulphide oxidation (Fig. 5A) in the medium created a high oxygen demand throughout the 65 days of the study, which was probably one of the factors limiting the DO increase in pore water (Glud 2008). Studies by Kemp et al. (2009) have shown that oxygen consumption during re-oxidation of anoxic sediments can be three times higher than the amount consumed under oxic conditions, thus delaying a return to optimum DO levels in the medium. Furthermore, in the last 15 days of the assay, when the rate of sulphide oxidation to sulphate was very high (Fig. 5A), the DO content remained constant (Fig. 3). These results corroborate with those obtained by Skoog and Arias-Esquivel (2009) on Long Island, since aerobic conditions were restored in the oxic layer of shallow sediment and water in a coastal area by means of oxygenation. These authors found that the percentage of dissolved oxygen increased as the sediment organic load and H_2S content decreased, and that the latter increased again when oxygenation treatment was interrupted.

A comparison of the progress of COD and OM content in the sediment samples showed that both parameters decreased in the same proportion (Figs. 4A and Fig. 6). Thus, after 25 days of OSSWI or AS treatments, sediment organic load was reduced by 73% and COD by 71%. These results suggest that COD was mainly generated by OM in the sediment. According to the marine sediment pollution index developed by Shin and Lam (2001), both Control and OSSWI-treated samples presented medium quality in regards to COD at the start of the assay and excellent quality after our 65 days experiment.

The results of this investigation have revealed that OSSWI and AS technologies were effective in remediation of marine sediments from sludge in a relatively short period of time. The mean difference between both technologies was the zone of influence during the remediation. Song et al. (2015) reported that the zone of influence during AS remediation is conical frustum shaped, so that, injected air migrates from the injection zone towards the top of the tank. These results that are in accordance with the fact that an effective remediation process has only been observed in the injection area and at 10 cm depth, while in areas located below the injector (30 cm depth), the effect of this technique has been minimal (Figs. 3B, 4B and 5B). On the contrary, the results suggest that OSSWI achieved a spherical diffusion into the marine sediment, allowing the remediation process along sediment profile to be similar (Figs. 3B, 4B and 5B).

5. **Conclusions**

This work demonstrates the efficiency of both OSSWI and AS technologies for remediating hypoxic marine sediments rich in OM that accumulates on beaches and other shallow coastal areas, under the laboratory condition used in this study. Results showed that in less than 25 days, these techniques transformed the initial sludge in a sediment with physicochemical characteristics that would make it suitable for hosting fauna from unaltered zones. The main advantage of these techniques compared to dredging is that OSSWI or AS methods could be applied *in situ* with minor environmental impact. Further research is required to optimize injection procedure and establish the efficacy of these methods at laboratory scale, although the good results obtained in this study suggest that it could be feasible to scale it to reality.

Among the two technologies studied, OSSWI was more effective in recovering the marine sediment from sludge than modified AS, because it allowed to recover the sediment in a wide area around the injection point.

In addition to the benefits obtained in hypoxic muddy sediments from shallow coastal areas, other application of these methods could include sludge extracted during port dredging, avoiding dumping of the dredged materials in landfills, which for legal and technical reasons entails substantial costs. OSSWI or AS are environmentally friendly technologies, since they prevent loss of coastal sand by enabling remediated, pollution-free sediments to be deposited along the coast.

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Conflicts of interests/Competing interests

The authors have no conflicts of interests to declare that are relevant to the content of this article.

Ethic approval

It is not applicable

Consent to participate/Consent to publish

It is not applicable

Research involving animals

It is not applicable

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Figures

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Fig. 3. (**A**) Variation of DO content ($mg\cdot L^{-1}$ at 25 ºC and 1 atm) in Air Sparging (AS) and Oxygen-Saturated Seawater Injections **(**OSSWI) treated pore water over time. Bars represent standard error. Different capital letters within AS treatment or different small letters within OSSWI treatment denote significant differences in DO content between different sampling times, according to Duncan's test ($p<5\%$). (**B**) Variation of the average DO content ($mg\cdot L^{-1}$ at 25 ºC and 1 atm) in AS and OSSWI treated pore water at the three depths studied. Bars represent standard error. Different letters within the different analyzed depths denote significant differences in DO content, according to Duncan's test ($p<5\%$).

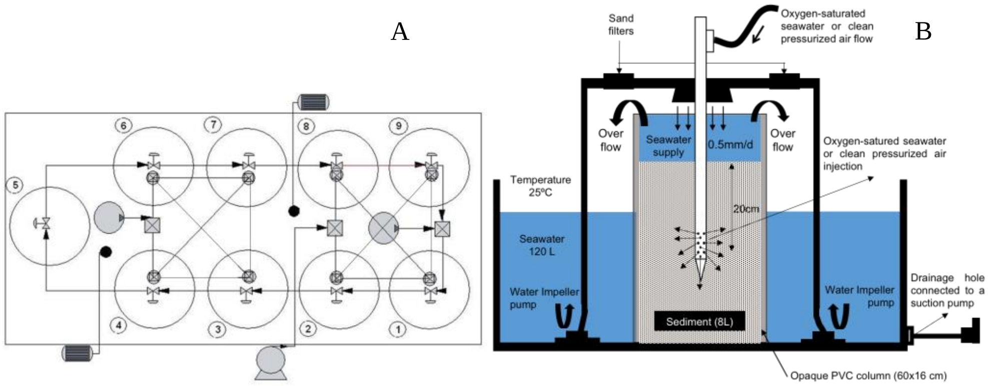
Fig. 4. **(A)** Variation of COD ($mg\cdot L^{-1}\cdot 10^3$) in Air Sparging (AS) and Oxygen-Saturated Seawater Injections **(**OSSWI) treated pore water over time. Bars represent standard error. (**B**) Variation of the average COD content ($mg\cdot L^{-1}\cdot 10^3$) in AS and OSSWI treated pore water at the three depths studied. Bars represent standard error. Different letters within the different analyzed depths denote significant differences in COD content, according to Duncan's test ($p<5\%$).

Fig. 5. **(A)** Variation of sulphate concentration ($g\cdot L^{-1}$) in Air Sparging (AS) and Oxygen-Saturated Seawater Injections **(**OSSWI) treated pore water over time. Bars represent standard error. Different capital letters

within AS or different small letters within OSSWI treatment denote significant differences in sulphate concentration between different sampling times, according to Duncan's test (p<5%). (**B**) Variation of the average sulphate concentration ($g \cdot L^{-1}$) in AS and OSSWI treated pore water at the three depths studied. Different letters within the different analyzed depths denote significant differences in sulphate content, according to Duncan's test (p<5%). Bars represent standard error.

Fig. 6. Variation of average organic matter content (%) over time for the two depths analyzed (10 and 20 cm). Bars represent standard error.

Fig. 7. Variation of average potential redox (mV) in Air Sparging (AS) and Oxygen-Saturated Seawater Injections **(**OSSWI) treated sediment over time. Bars represent standard error.



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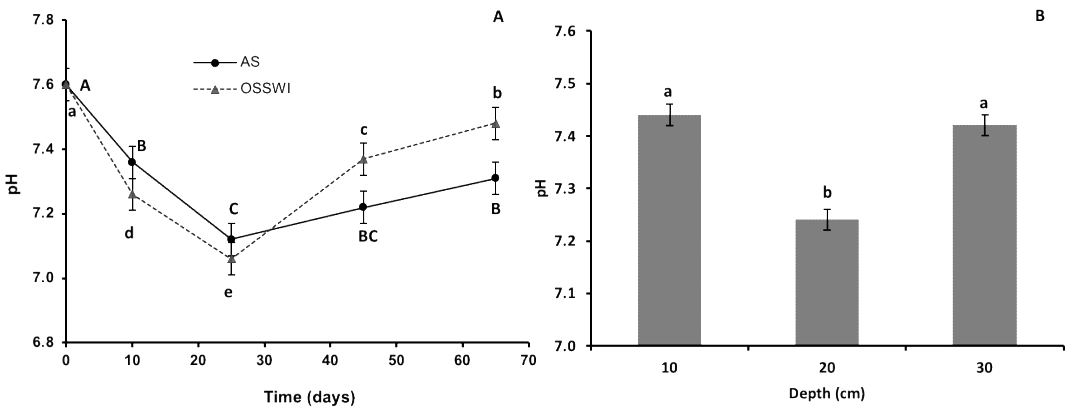

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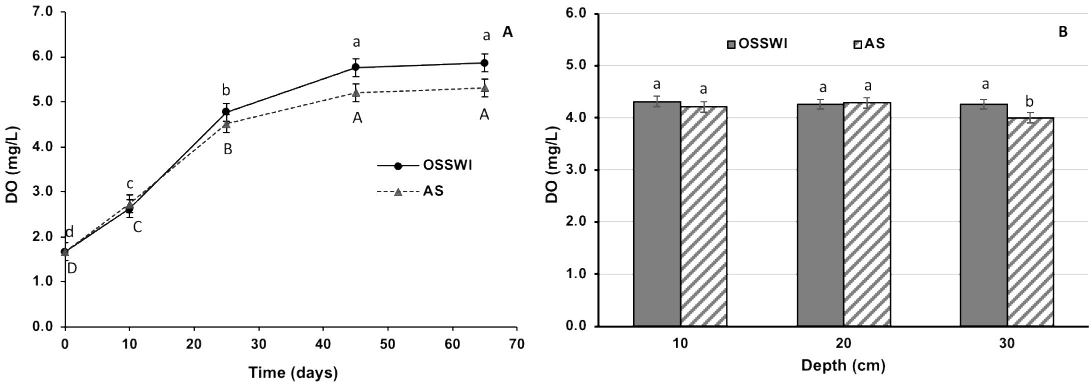

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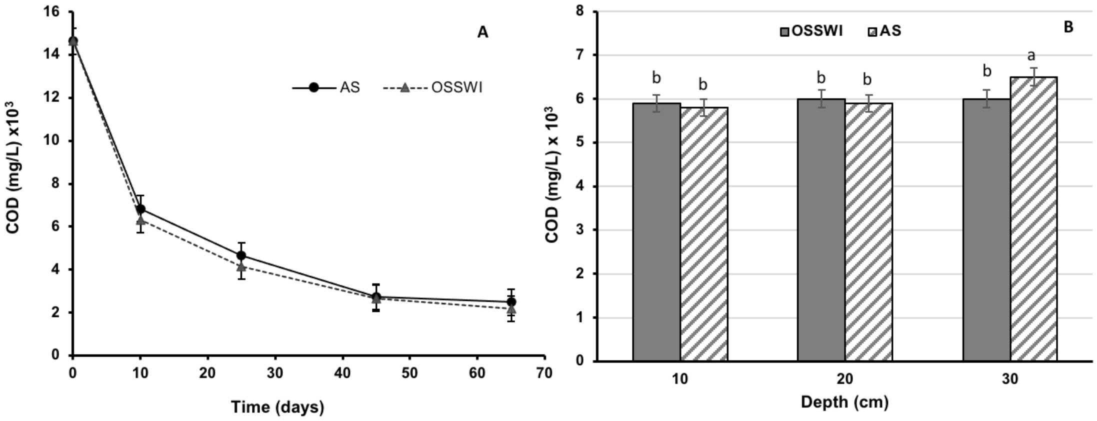

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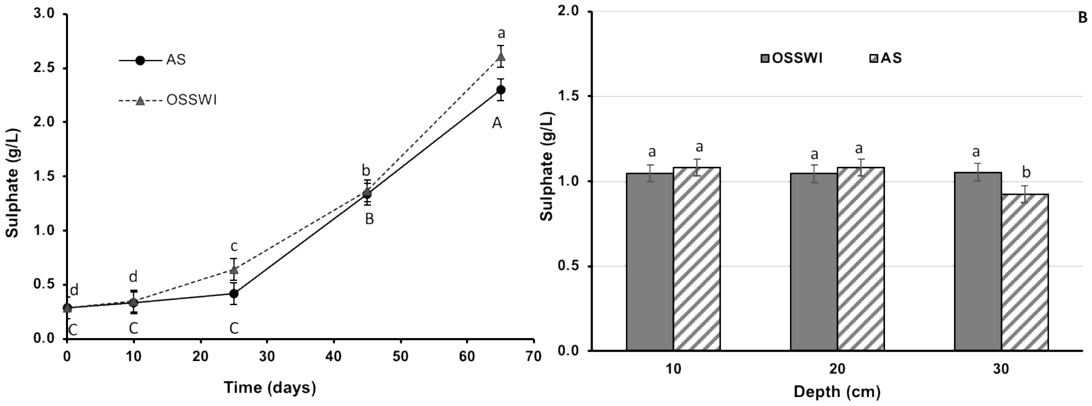

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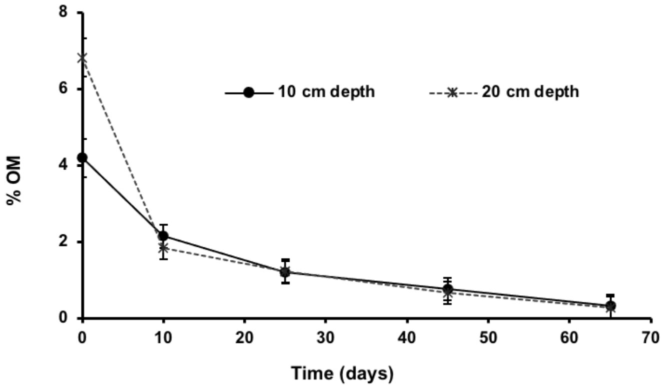

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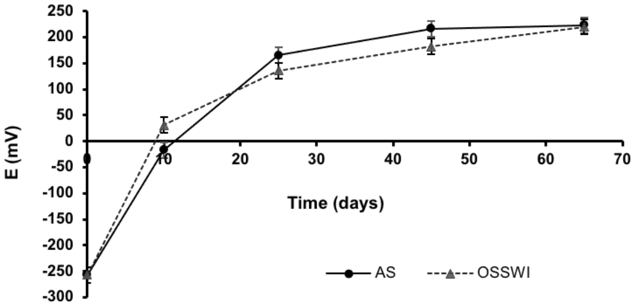

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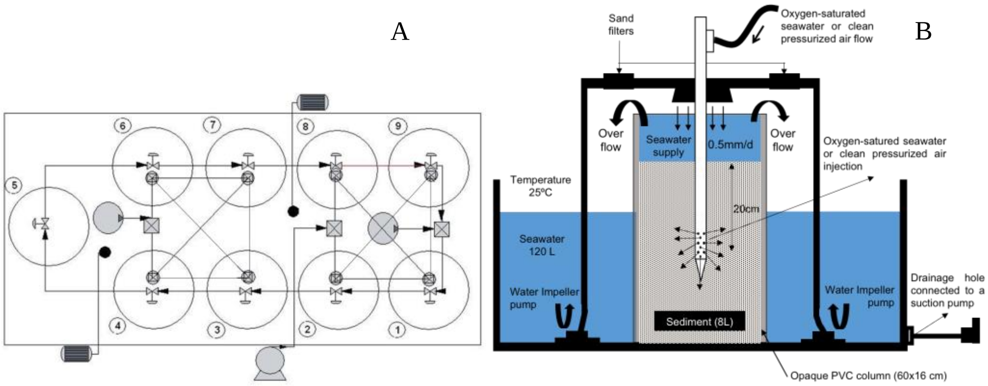
Tables

Table 1. ANOVA p-values for the three fixed factors and their double and triple interactions for temperature (TEMP), salinity (EC), pH, dissolved oxygen (DO), chemical oxygen demand (COD), sulphate concentration ([SO_4^{2-}]), organic matter (OM) and redox potential (E).

Factors	TEMP	EC	pH	DO	COD	[SO_4^{2-}]	OM	E
[T]	0.742	0.983	0.138	0.019	0.168	0.031	0.498	0.074
[D]	0.129	0.956	0.001	0.022	<0.001	<0.001	<0.001	--
[P]	0.356	0.539	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
TxD	0.780	0.942	0.543	0.038	<0.001	<0.001	0.766	--
TxP	0.642	0.790	0.006	<0.001	0.981	0.001	0.093	<0.001
DxP	0.345	0.621	0.447	0.009	0.058	0.130	<0.001	--
TxDxP	0.924	0.986	0.669	0.723	0.394	0.115	0.317	--

p>0.05 no significative. Fixed Factors: [T]: Treatments: AS and OSSWI treatment; [D]: Depth: cm from the top of sediment; [P]: Treatment period: in days.



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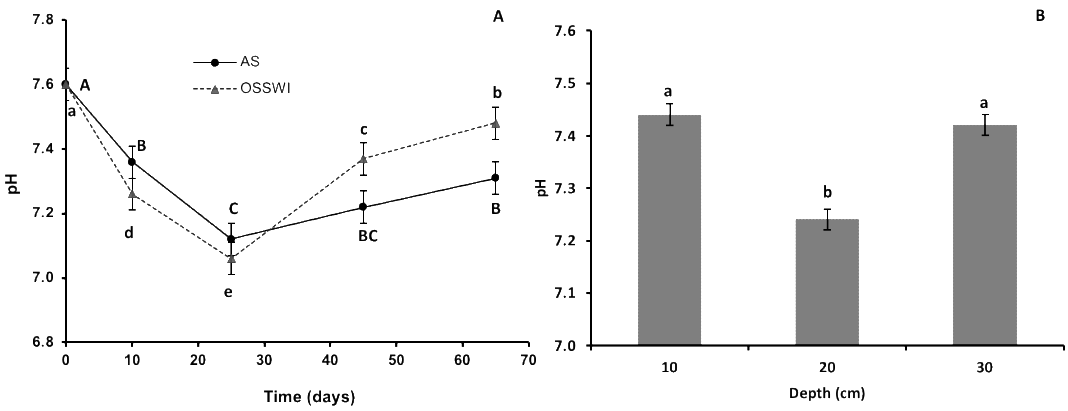


Fig. 2. (**A**) pH variation in modified Air Sparging (AS) and Oxygen-Saturated Seawater Injections **(**OSSWI) treated pore water over time. Bars represent standard error. Different capital letters within AS treatment or different small letters within OSSWI treatment denote significant differences in pH between different sampling times, according to Duncan's test (p<5%); (**B**) Relationship between pH and depth. Bars represent standard error. Different letters within the different analyzed depths denote significant differences in the pH, according to Duncan's test (p<5%).

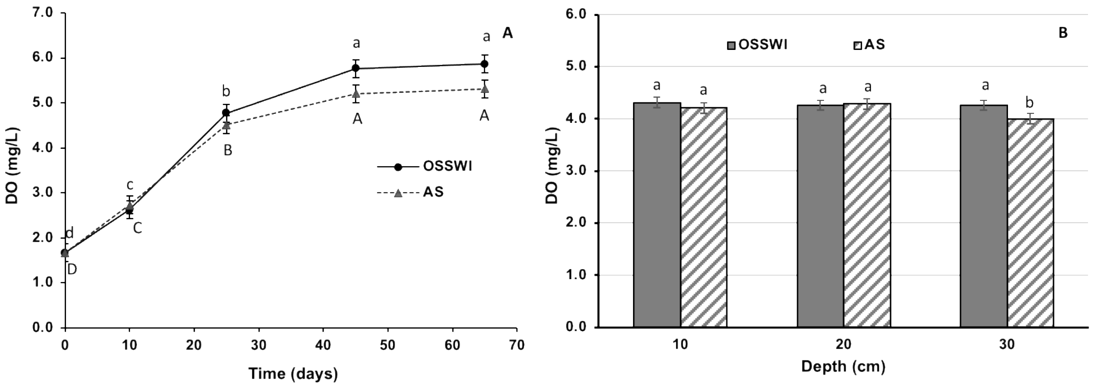


Fig. 3. (**A**) Variation of DO content (mg·L^{-1} at 25 ºC and 1 atm) in modified Air Sparging (AS) and Oxygen-Saturated Seawater Injections **(**OSSWI) treated pore water over time. Bars represent standard error. Different capital letters within AS treatment or different small letters within OSSWI treatment denote significant differences in DO content between different sampling times, according to Duncan's test ($p<5\%$). (**B**) Variation of the average DO content (mg·L^{-1} at 25 ºC and 1 atm) in AS and OSSWI treated pore water at the three depths studied. Bars represent standard error. Different letters within the different analyzed depths denote significant differences in DO content, according to Duncan's test ($p<5\%$).

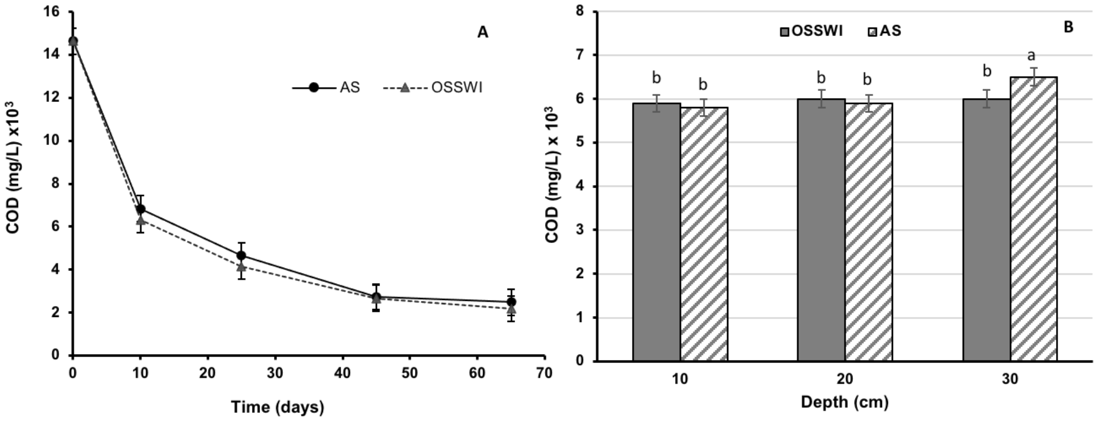


Fig. 4. **(A)** Variation of COD ($mg\cdot L^{-1}\cdot 10^3$) in modified Air Sparging (AS) and Oxygen-Saturated Seawater Injections **(**OSSWI) treated pore water over time. Bars represent standard error. (**B**) Variation of the average COD content ($mg\cdot L^{-1}\cdot 10^3$) in AS and OSSWI treated pore water at the three depths studied. Bars represent standard error. Different letters within the different analyzed depths denote significant differences in COD content, according to Duncan's test (p<5%).

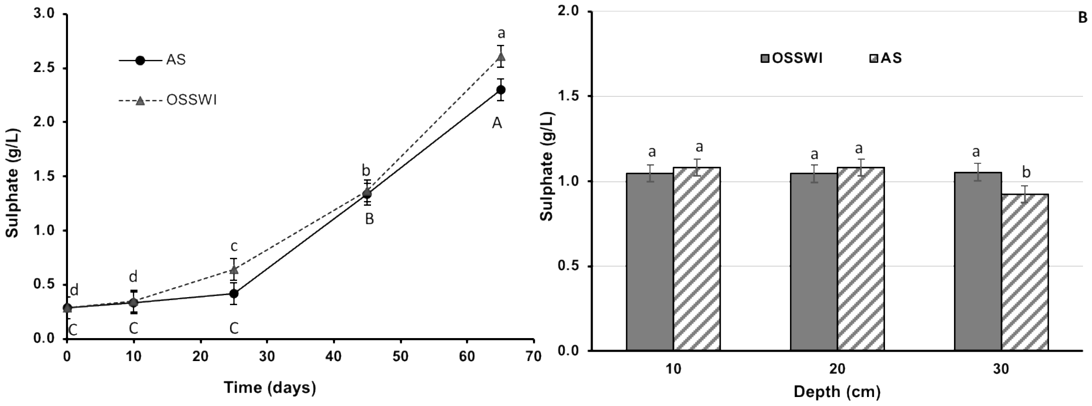


Fig. 5. **(A)** Variation of sulphate concentration (g·L^{-1}) in modified Air Sparging (AS) and Oxygen-Saturated Seawater Injections **(**OSSWI) treated pore water over time. Bars represent standard error. Different capital letters within AS or different small letters within OSSWI treatment denote significant differences in sulphate concentration between different sampling times, according to Duncan's test ($p<5\%$). (**B**) Variation of the average sulphate concentration (g·L^{-1}) in AS and OSSWI treated pore water at the three depths studied. Different letters within the different analyzed depths denote significant differences in sulphate content, according to Duncan's test ($p<5\%$). Bars represent standard error.

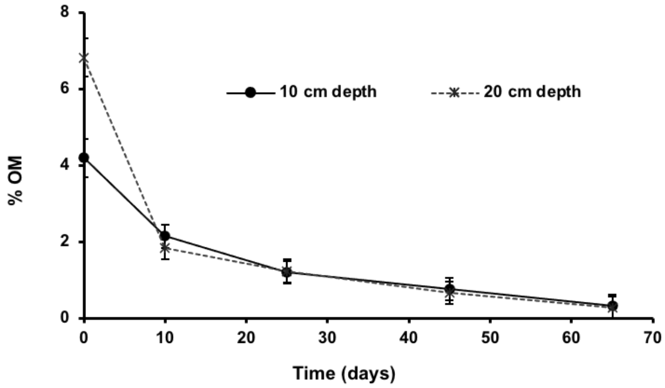


Fig. 6. Variation of average organic matter content (%) over time for the two depths analyzed (10 and 20 cm). Bars represent standard error.

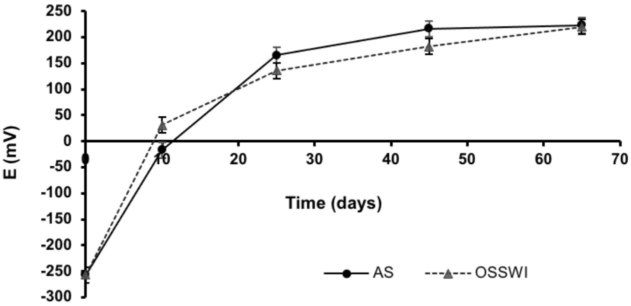


Fig. 7. Variation of average potential redox (mV) in modified Air Sparging (AS) and Oxygen-Saturated Seawater Injections **(**OSSWI) treated sediment over time. Bars represent standard error.

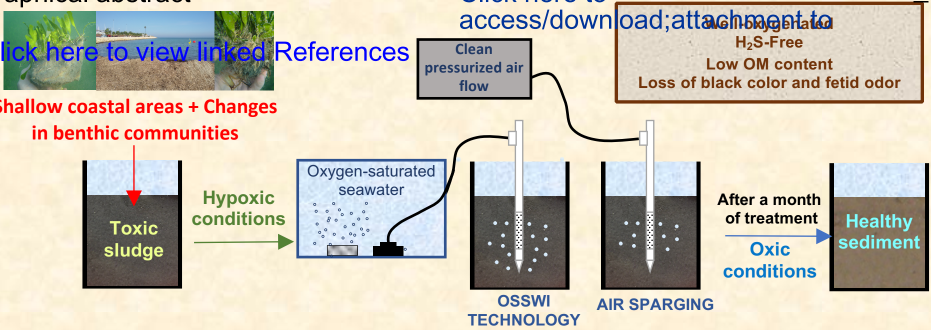
Tables

Table 1. ANOVA p-values for the three fixed factors and their double and triple interactions for temperature (TEMP), salinity (EC), pH, dissolved oxygen (DO), chemical oxygen demand (COD), sulphate concentration ($[SO_4^{2-}]$), organic matter (OM) and redox potential (E).

Factors	TEMP	EC	pH	DO	COD	$[SO_4^{2-}]$	OM	E
[T]	0.742	0.983	0.138	0.019	0.168	0.031	0.498	0.074
[D]	0.129	0.956	0.001	0.022	<0.001	<0.001	<0.001	--
[P]	0.356	0.539	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
TxD	0.780	0.942	0.543	0.038	<0.001	<0.001	0.766	--
TxP	0.642	0.790	0.006	<0.001	0.981	0.001	0.093	<0.001
DxP	0.345	0.621	0.447	0.009	0.058	0.130	<0.001	--
TxDxP	0.924	0.986	0.669	0.723	0.394	0.115	0.317	--

$p > 0.05$ no significative. Fixed Factors: [T]: Treatments: AS and OSSWI treatment; [D]: Depth: cm from the top of sediment; [P]: Treatment period: in days.

graphical abstract



Shallow coastal areas + Changes in benthic communities

Toxic sludge

Hypoxic conditions

Oxygen-saturated seawater

Clean pressurized air flow

OSSWI TECHNOLOGY

AIR SPARGING

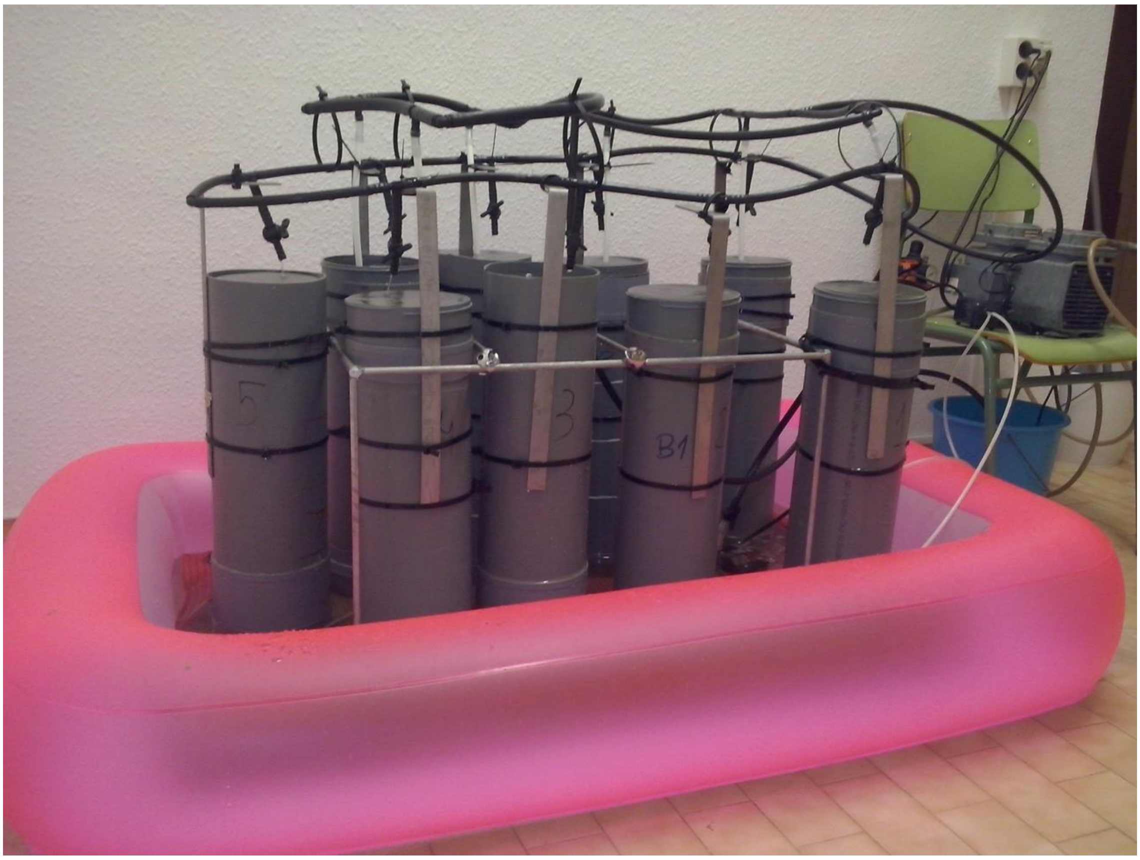
After a month of treatment

Oxic conditions

Healthy sediment

Well-oxygenated
H_2S-Free
Low OM content
Loss of black color and fetid odor

pictures experimental setting

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Effectiveness of Oxygen-Saturated Seawater Injections and Air Sparging Technologies in Remediation of Coastal Marine Sediments from Sludge

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COMMENTS FOR THE AUTHOR:

Reviewer #1:
The ms entitled "Effectiveness of Oxygen-Saturated Seawater Injections and Air Sparging Technologies in Remediation of Coastal Marine Sediments from Sludge" brings the comparison between two techniques for sediments remediation. Although the foundations of both techniques are quite similar, the OSSWI seems to be a promising tool if correctly implemented.
It is somewhat unfortunate, however, that the ms is rather confusing describing the experiments performed, with no well-defined hypothesis, experimental design not enough explained, poorly written results with English needing a thorough review, particularly the grammatical tense coherence along the ms.

The manuscript has been thoroughly revised to improve all aspects indicated by reviewer #1. Please, check the changes made to the manuscript.

The introduction opens expectations not fulfilled in the following sections. It is written focused on sediments remediation in beaches for recreation activities, but only a lab experiment has been performed. The statement in line 112 that "the goal of this study was to compare the effectiveness of both technologies to improve the physicochemical properties of coastal sediments and to enhance conditions for recreational use of shallow beaches" is not in accordance with the experiment performed not even at pilot scale in the field. Did the authors perform a larger experiment in the field? What would be the infrastructure needed to scale the obtained results? Would that be doable to larger scales?

The introduction and aims of the study have been modified to be consistent with the laboratory-scale research that has been performed. Please, see the manuscript

The schematic sketch of the system in Fig 1 needs to be completed with a photograph of the system in order to provide a clear and precise idea of what and how the experiment was performed.

The schematic drawing of the experimental setting (Fig 1) has been completed and pictures of the experimental system has been included in the supporting information section.

Lines 127 to 131 needs be rephrased to better and clearly understand the procedure. It is stated that experimental conditions were simulating natural conditions but no measurements of any natural condition is reported.

The sentences in lines 127 to 131 have been rewritten and information about the natural sea conditions at Marineta Casiana beach have been included. Please, see the manuscript.

Experimental design must be clearly stated from the beginning, only at the end of the section the reader realize that 4 cores were used for AS, another 4 for OSSWI and another 4 for control.

The distribution of the cores according to the applied treatment has been included at the beginning of materials and methods section. Please, see the manuscript.

No reference of control results is made along the ms.

The aim of the study was to compare the efficacy of the two techniques (AS and OSSWI) for remediating sludge in coastal sediments. The control was only used to confirm that the parameters studied (temperature, salinity, pH, DO content, COD, sulphate concentration, %OM and redox potential) remained constant in the untreated samples throughout the trial, i.e., with similar values to those determined at initial sampling time (time 0)).
The control was not included in the factorial analysis of variance. For the fixed factor Treatment, only AS and OSSWI were considered. Please, see the manuscript.
For all these reasons, the control is not cited in results and discussion sections.

It is not clear whether water was directly pumped from the sea to the container every 15 days and then used in the system or directly pumped to the whole system. It would be much useful to add a picture of the pipe and mesh tube to Fig 1 (Line 147)

The water was directly pumped from the sea to the container every 15 days and then, used in the system. The sentence has been rewritten. Please, see the manuscript.

Line 181 - delete second time "treatment"
The change has been made in the manuscript. Please, see ms

Line 183 - is %DO the percentage of saturation or mg/L? state clearly.
In the manuscript, DO content has been expressed as mg/L. The manuscript has been revised and the units of DO concentration have been unified. Please, see the manuscript.

Meaning of letter in Figures 2 to 5 is not clear and need further explanation, neither explanation given in figures caption.
The explanation in the figures caption has been included. Please, see the manuscript

Reviewer #2: Authors have presented a good article related to the possibilities of solving a real problem in many areas, but specially un touristic areas like these, in the Mediterranean sea.
The importance of this article is more than that related to recover recreational areas. I think that this can be also applied to recover natural areas affected by wastes that can produce hypoxic muddy sediments.
Although it is a lab experiment, the results are promising and can be useful to proceed to design an experiment in the site. However, this process needs later an economic feasibility study.
The article is, in my opinion, well written and organized, and materials and methods, results and discussion are adequate and length satisfactory. The problem of this type of hypoxic muddy sediments in touristic areas is great because of the rejection produced to the visitors.
Please check the following possible mistakes:
Page 4, line 90. The reference given is "European Comission 2000", please confirm if this reference is the same given in REFERENCES "European Waste catalogue 2000" or is a missed reference.
It was an error, and the reference has been changed.
Page 11, lines 322, 324 and 325, the units of the data given are cut by the end of the line. I know this not a mistake but some attention should be given during editing process.
Thank you for your appreciation, we will pay attention to the details so that this error does not occur.