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ARTICLE

Internal Waves Formation and Propagation in the Persian Gulf

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ABSTRACT

The Persian Gulf (PG), as a semi-enclosed water basin extends in [47-57] E, [24-30] N, geographic domain. Particularly, northern part of the PG shows more baroclinicity and turbulence because of the river inflow from the Arvand, bottom and costal stresses. Furthermore, wind stress has many effects rather than in mid deep domain of the PG. Thermocline development in the PG is observed because of studying the data measured in the Mt. Mitchell cruise in 1992 by different models from winter to summer. The studied turbulence in the northern part of the PG is navigated from winter to summer due to the internal wave's activity and stability intensified through water column.

1. Introduction

Internal waves play a major role in the formation of seawater stratification and are responsible for the main processes of ocean dynamics, such as energy transfer and mixing [8]. The surface layer is influenced by local wind forcing. The thermocline tries to re-stabilize itself after the cessation of dry season and oscillates for the rest of the year. A main source of turbulence energy is the internal wave field. Some of internal wave energy derives from the transmission of wind energy through the surface mixed layer [1]. The measurement stations in the PG are presented in Figure 1.

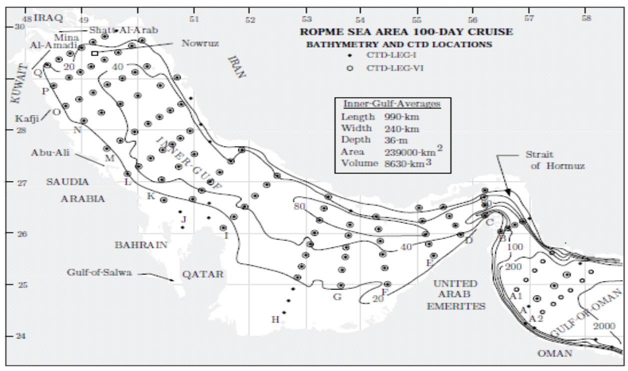

Figure 1. Aero picture of the PG showing measurement stations in three measuring sections

(Northwestern, mid deep and near the Strait of Hurmoz)

An important mechanism for exiting fields of internal

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gravity waves (IGW) in natural (ocean, the Earth atmosphere) and artificial stratified media is their generation by sources of perturbation of various physical nature, i.e., of natural (moving typhoon, wind waves, flow past the ocean bottom relief imperfections, variations in the density and flow fields, leeward mountains) and anthropogenic) marine technological structures, collapse of the turbulent mixing region, underwater explosions(character [6]. As a result of variations of physical characteristics of PG water through column, and effects of climate on the water surface, internal waves happen and vary in water column of PG. Therefore, study of the waves in the PG water column has an importance we concentrate in this paper including results of a research.

2. Thermocline Formation in the PG

Thermocline forms in the PG, and this is a seasonal phenomenon because of particularly temperature variation through water column in the PG. Therefore, thermocline will be studied in this research according to data collected during Mt. Mitchel cruise in the PG, curves contours are drawn in Figure 2 to Figure 6. Temperature, density and salinity are three useful physical properties of seawater to studying. Naturally, the temperature of seawater is fixe at the surface by heat exchange with the atmosphere. Temperature and density vertical variations in some stations in three measurement sections are as in the following profiles in the PG in winter and summer.

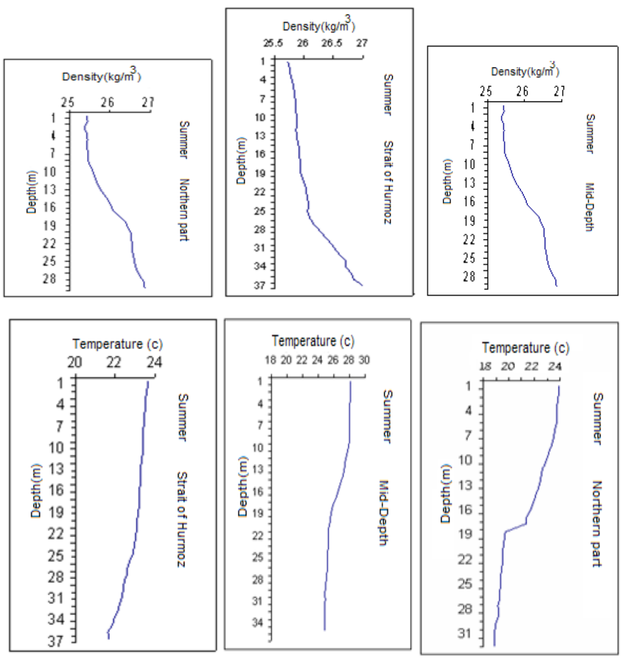

Figure 2. Vertical variations of temperature and density in three measurement sections in the PG, winter and summer 1992

The atmospheric disturbance is set by an idealized pulse of cyclonic wind stress with a Rankine vortex structure. Strength, radius and duration of the forcing are varied. The effect upon wave generation of stratification with variable mixed-layer depth is also examined [9]. Relying on the accuracy of the curves in Figure 2, it could be stated that vertical gradient of temperature and density in the subsurface of the water column is very high in the summer but in winter, it is high only in the Strait of Hormuz because of water exchange in winter.

In fact, it could be resulted that thermocline exists only in summer. Overall, the temperature breaks in the subsurface layer through the water column because of wind stress, demonstrates the thermocline developed in the study area. In this regard, thermocline formation and its development are associated to some variations in internal waves, particularly in subsurface layer.

In fact, thermocline development and its variation in space and time represent a turbulent flow, and thus propagation of internal waves through water environment. Turbulence and internal waves propagate along the baroclinic pressure gradient in a vertical direction through the water column due to baroclinicity and tidal wind stress [10]. Based on Figure 2 comparing the curves, we could observe that thermocline does not form in winter, particularly in the Strait of Hormuz because of water exchange with the Gulf of Oman. However, it forms all over the PG through the water column, suggesting that thermocline develops from the Strait of Hormuz to the PG North from winter to summer.

3. Results and Discussion

The point is that internal waves can create rather strong currents on the ocean surface. The flow is changed depending on the wave extension: its velocity is greater at the wave crest and wave trough, and is slower where thermocline oscillations are little [7]. Internal waves in PG in summer differ from winter, due to differences of forcing and factors in summer and winter. Internal waves breaking results in turbulence propagation during winter to summer [2]. Arvand river inflow in northwestern of the PG helps to stratification, and then internal waves and turbulence can form there. Of course, the gradient throughout density contours throughout the PG represents the existence of the internal waves due to thermocline formation, particularly in summer because of high intensity forcing. Wind stress affects the PG surface in the following processes:

(1) An atmospheric disturbance causes an internal wave.

(2) Turbulence is driven by internal waves shear.

(3) Vertical density fluxes are resulted from the mixing.

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(4) A gravitational imbalance in the horizontal direction includes an intrusion.

(5) High wave number internal waves are generated at the head of the intrusion.

Wind stress as a forcing generates an acceleration for water body in vertical and horizontal directions with its components due to shear induced on water [5].

Thermocline forms in the open ocean and can be a seasonal phenomenon in the shallower part of the ocean or a permanent since it is seen in the deeper part of the open ocean. Thermocline is a phenomenon which happens in the Persian Gulf., and it develops from winter to summer resulted of the numerical model (POM) in the PG[3]. Formation of a shallow thermocline with upper mixing and displacements of the thermocline is associated with internal wave propagation, which plays an important role in turbulence generation. The stratification as an important factor influencing on local generation of internal waves in the coastal zones subjected to seasonal variability [4].

In this study, we have wanted to appoint internal waves dependence on thermocline development in the PG, and so will conclude internal waves and turbulence. As in the above profiles, there are fluctuations and variations along vertical T & D; therefore, it could be a crucial result of internal wave's existence. Thus, thermocline development often causes turbulence. We could express that turbulence happens in the PG, because of some forcing all over the PG, such as: tide, wind stress, river inflow. In the PG, baroclinic pressure happens in various stations as in the last profiles. Buoyancy frequency (Brunt Vaisala) as following as baroclinicity and density gradients received by a code in FORTRAN in some stations in regards to turbulence and internal wave's existence are drawn against depth. Figure 3 shows vertical variations of buoyancy frequency in two measurement sections. In fact, in most of the measurement stations, internal waves could form.

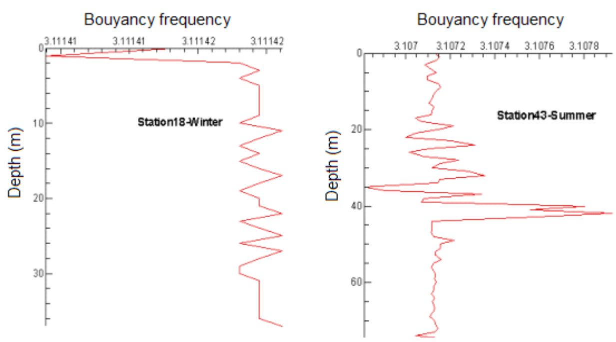

Figure 3. Buoyancy frequency N (z) (* 0.01) in some important stations in summer and winter 1993, winter and summer 1992

In fact, more variations through the buoyancy frequency happen in summer rather than in winter, because of more gradients in T and D. The buoyancy frequency is calculated as in the following:

$$N(z)^2 = (-g/\rho)(\Delta\rho/\Delta z) \qquad (1)$$

Where w, N (z), w and p (z) are vertical component of internal wave velocity, wave number velocity and mean density function in water column. Depth mean variations for internal wave's velocity (vertical component) profiles in the PG is received as in Figures 4 and 5 in summer and winter with and without bottom stress.

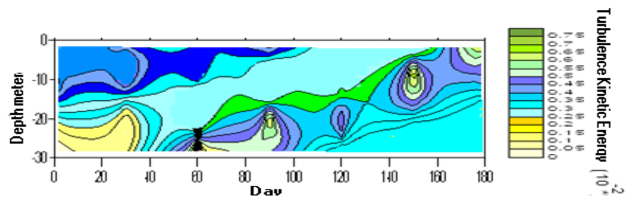

Figure 4. Mean TKE through the PG during winter until summer

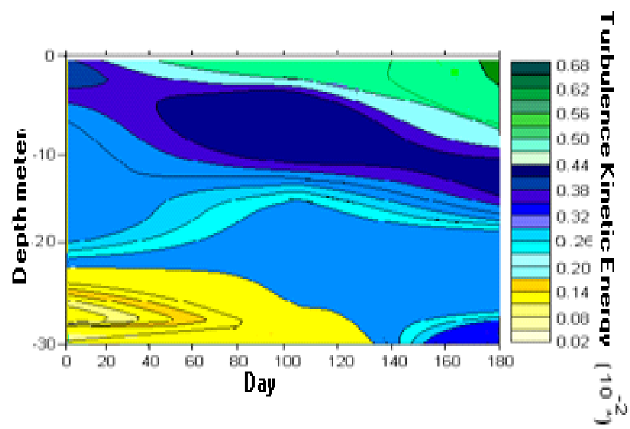

Figure 5. Mean TKE through the PG during winter until summer without bottom stress, winter and summer 1992

In figure 6, profiles of vertical component of internal wave velocity in some points of the PG in winter and summer 1993 depth (m) against velocity (m/s) are showing turbulence in summer because of thermocline develops from winter.

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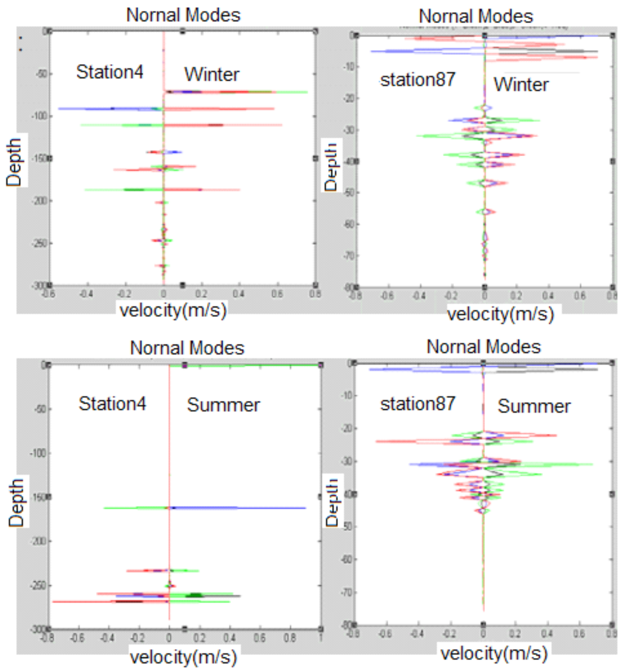

Figure 6. Internal wave's velocity variations in some stations in the Persian Gulf in winter and summer, winter and summer 1992

As it could be seen, internal wave's velocity variations in z direction are more in summer rather than in winter, because of thermocline fluctuations based on much density variations.

4. Conclusion

Existence of stratification and development of thermocline in the PG is a crucial phenomenon. Summer thermocline formation in the PG is a seasonal potential of turbulence, and internal wave's creation would happen in the case study zone. Thermocline formation is usually associated with internal waves as an important cause in turbulence.

Internal waves are able to provide and transmit the energy, which is essential for aquatic circulation and mixture. Moreover, in coastal areas that charges in fluid temperature in water column causes diffusion of internal waves.

It could be concluded that:

(1) Baroclinic pressure and stratification, cause turbulence throughout PG water column in summer.

(2) In summer, turbulent behavior happens. The most effective factors on the behavior in the PG are tide, wind, evaporation and river inflow.

(3) The existence of tides, northwestern winds and strong internal waves in PG results in high vertical component of internal wave's velocity.

(4) Turbulence and internal waves due to baroclinic pressure because of density gradients exist in the PG water in summer.

(5) Vertical component of internal waves velocity has range of [-0.8, +0.8] with more fluctuations in summer.

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ARTICLE

Biochemical Composition and Anticancer Effect of Different Seaweed Species (*In-vitro and In-vivo* Studies)

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ABSTRACT

Seaweed is an enormous resource comprised with natural bioactive compounds with several therapeutic effects including anticancer activity. In this context, the biochemical composition of seaweed plays a major role. Many biochemical compounds isolated from seaweed, fractions of seaweed and crude extracts has revealed ability of seaweed to fight against several cancer types. In this contrast seaweed extracts inhibit cancer cell growth and proliferation by inducing apoptosis and by inhibiting metastasis activity. In this review, biochemical and anticancer properties of seaweeds are discussed and this will provide the basic information to develop a novel chemotherapeutic drug to challenge the cancers.

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1. Introduction

Cancer is a dreadful disease causes due to uncontrolled cell proliferation and migration [17,26]. Among all human cancer types, lung cancer and colorectal cancer are the major cancers found in male whereas breast cancer, cervical cancer and lung cancer are considered as the common cancers found in female [1,40]. Although chemotherapy and radiotherapy treatments are practiced to cure cancers, the survival rate is still low and many side effects are also reported [23]. Due to the continuing of failure of the availability of effective chemo-preventive agents for cancers, therapeutic agents from biological resources are being experimented to control this malignant disease [8,11,18]. Seaweeds are marine macro algae, found in intertidal and sub-tidal zones and classified based on their pigmentation and chemical composition as Chlorophyta (green algae), Rhodophyta (red algae) and Phaeophyta (brown algae) [6,23]. *Laminaria* sp., *Fucus* sp., *Ascophyllum* sp., *Porphyra* sp., *Ulva* sp., *Sargassum* sp. and *Gracilaria* sp. are some of the examples for the famous edible seaweed species that comprise with many bioactive compounds coming under the groups of polysaccharides, proteins, lipids, minerals and vitamins [14,1]. Moreover, due the availability of theses bioactive compounds many seaweed species account for promising health promoting effects such as antibacterial, antiviral, anti-inflammatory, antiulcer and anticancer activities [1,13,33,41]. Therefore some secondary metabolites in seaweeds are extracted and incorporated into several products such as foods, medicines and cosmetics [5]. Recently, seaweeds are increasingly being considered as a source with effective anticancer agents that are able to lower the risk of cancer [1,17,26]. In this context, investigation of anticancer drugs with less or no side effects has become an interesting topic in novel research field [37,43].

2. Biochemical Composition of Seaweeds

There are two types of biochemical substances present in seaweeds as high molecular materials and low molecular materials. High molecular materials such as dietary fibres are not absorbed into the human body whereas low molecular materials are absorbed directly [14]. Though seaweeds comprise with several biochemical compounds including carbohydrates, proteins, lipids, vitamins, polyphenols, free amino acids and minerals [7,14,24] the composition varies based on the geographical location, seasonal variation and water temperature [14,24].

Seaweeds contain 20% - 76% (dry weight) of polysaccharides as structural and storage compounds. Cellulose, starch, hemicellulose, fucoidan, alginic acids, Sulfated fucans, alginate and laminarin are the polysaccharides which are mainly present in the seaweeds that provide strength and flexibility to the cell wall [5,13,14]. Out of three seaweed types red seaweeds consist with the highest protein content which accounts for 30%-40% of dry weight whereas brown seaweeds contain 15% and green seaweeds contain 30% of dry weight [34]. Many essential amino acids, such as glycine, alanine, arginine and glutamic acids are present in seaweeds. However, the lipid content of seaweeds is comparatively low (1%-5% of dry weight) and it contains a high proportion of essential fatty acids and poly unsaturated fatty acids such as ω-3 and ω-6 [30]. Vitamin B, C, A and D are the most common vitamins present in the seaweeds. In general, seaweeds accounts for 36% (dry weight) of minerals including, potassium, sodium, magnesium, calcium, sulfur, chlorine, phosphorus, iron, zinc, iodine, copper and some other trace metals [34]. Several studies reported that there are severel types of secondary metabolities with therapeutic effect are present in seaweeds (Table 1)

Table 1. Secondary metabolites in seaweeds

Family	Seaweed Species	Secondary Metabolites	Reference
Pheophyta	*Fucus vesiculosus* *Fucus evanescens* *Ascophyllum nodosum* *Undaria pinnatifida* *Sargassum thunbergii* *Ecklonia cava*	Fucoidan	[3,13,16, 20,32,39,45]
	Laminaria sp.	Laminarin	[13,31]
	Sargassum heterophyllum *Laminaria ochotensis* *Hijikia fusiformis* *Undaria pinnatifida* *Ectocarpus siliculosus*	Fucoxanthin	[2, 25, 38]
Chlorophyta	*Nitella Hookeri* *Ulva fasciata*	Flavonoids	[31]
	Laurencia glandulifera	Dactylone	[10]

3. Anticancer Effect of Seaweeds

Uncontrolled cell growth and proliferation is the main reason for cancer formation. Chemo-preventive agents extracted from natural resources have got the attention due to the ability to suppress cancer cell formation with lesser or no side effects with compared to available chemotherapeutic agents [20]. Basically, cell death can be caused by any chemotherapeutic agent through the cell

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cycle arrest by targeting necrotic pathway or apoptotic pathway of respective cells [23,26]. Bioactive compounds are able to induce apoptosis in cancer cells, this is one of the key mechanisms in cancer therapy because apoptosis is a kind of programmed cell death which can kill only the targeting cancer cells without causing damage to normal surrounding cells [2,40]. In this context, cell death is evoked through intrinsic mitochondrial pathway or extrinsic death receptor pathway [23,40]. Several studies have proven that seaweed constitute many novel bioactive compounds with anticancer effect and able to induce apoptosis in several types of cancer cells [1,3,9,13,35,37].

Anticancer effect of methanolic extract of *Caulerpa racemosa* mentioned was examined against HL-60 (Human promyelocytic leukemia) cell line and a remarkable cell growth inhibition was reported by Lakmal, *et al.*, 2014 [21] in dose - dependent manner with compared to normal cell line; vero (Monkey kidney cell line). Apoptotic body formation and DNA damage of treated HL-60 cancer cells were obsereved under fluorescent microscopy and flow cytometric analysis was also showed dose dependent sub-G1 DNA accumulation in HL-60 cell line. Aqueous and methanolic extract *Kappaphycus striatum* has showed cell growth inhibition activity against HeLa (Cervical adenocarcinoma) cell line and this study explains that the molecular weight, monosaccharide sequence, bond formation and charge of molecules are the characteristics of bioactive compounds present in seaweed extracts which support seaweeds to act as an anticancer agent [22]. Zandi, *et al.*, 2010 [42] has found that the aqueous extract of *Sargassum oligocystum* shows cytotoxic activity on K562 (Human chronic myelogenous leukemia) and Human Daudi (Burkitt Lymphoma) cell lines in dose dependet manner. Moreover by another study Zandi, *et al.*, 2010 [43] expalins that the aqueous extract of *Gracilaria corticata* filtered with Whatman paper No.1 filter paper showed more pormising cell growth inhibition results on Jurkat and Molt-4 (Human lymphoblast) cell lines and they emphasis that filtration is the one of the best methods of sterilising the seaweed extarcts since some of the bioactive compounds in seaweeds are heat sensitive. MCF 7 (Human breast adenocarcinoma) cell line treated with aqueous extracts of different seaweed species such as *Gracillaria corticata, Ulva fasiata, Chaetomorpha antennina* showed growth inhibitory effect and morphological observation such as cell shrinkage and cell shape changes related to apoptotic induction were also observed [4].

Methanolic extract of *Sargassum muticum* has showed antiproliferative activity by inducing apoptosis in MCF-7 (Human breast adenocarcinoma) cell line. Electron microscopic images with membrane blebbing, apoptotic body formation and microvilli reduction, the morphological changes of treated cells stained with Hoechst 33342 and flow cytometric analysis indicating the accumulation of treated cells at sub-G1 phase provide evidence on inducing apoptosis by Methanolic extract of *Sargassum muticum* [28]. MCF-7 (Human breast cancer cell line) and HepG2 (Human liver cancer cell line) treated with methanolic extracts of *Enteromorpha antenna, Gracilaria corticata* and *Enteromorpha linza* has shown cytotoxic activity with compared to normal Vero cell line (Monkey kidney cell line) [29]. Gomes, *et al.*, 2015 [12] found the Methanolic extracts of *Dictyota cilliolata* and *Dictyota menstrualis* shows dose-dependent and time-dependent antiprolifertive effect on HeLa (Human cervical cancer cell line). Nuclear morphology changes such as formation of apoptotic bodies and chromatin condensation in the cells stained with 4, 6-Diamidino-2-phenylindole (DAPI) staining was observed under fluorescent microscope. It is reported that percentage of annexin-positive (annexin V-FITC+/PI−) cells Flow was increased and it is a sign of early apoptosis process of cells. Further the results highlighted that the methanolic extracts of *Dictyota cilliolata* inhibits the growth of HeLa cells by blocking the cell cycle at the S phase whereas *Dictyota menstrualis* shows apoptotic induction without inducing cell cycle arrest. Caspase 3 and Caspase 9 activation empahasis that intrinsic apoptotic induction occurs by the seaweed extracts in the cancer cells. Ethanol extract of *Ulva fasciata* has showed growth inhibition due to apoptosis induction HCT 116 (Human colon cancer) through mitochondrial pathway by increasing cell at sub-G1 phase and activation of Caspase 3 and Caspase 9 [36].

Fractions of polysaccharides; SP-3-1 and SP-3-2 extracted from *Sargassum pallidum* were treated on HepG2 (human hepatoma), A549 (human lung cancer) and MGC-803 (Human gastric cancer) cell lines and evaluated by MTT assay. SP-3 fraction with the highest sulfate content exhibited higher antitumor activity against all tested cancer cell lines. Further, this study states structure, glycosidic linkages and sequence of monosaccharaides effects on the function of the extracted polysaccharides [41]. Anticancer effect of a sterol fraction of *Porphyra dentata* was evaluated against 4T1 breast cancer cell line and pronounced in dose dependent and time dependent cell proliferation inhibition of was resulted in the treated 4T1 cells and percentage of apoptotic-necrotic cells increased was also increased due to the results of PI and annexin V dual staining [19]. Liu *et al.* (2016) [23] evaluted the anticancer effect of a

Table 2. Anticancer activity of different seaweed extracts

Extract type	Seaweed Species	Cancer cell type	*In-vitro* analysis				References
			MTT Assay	Morphological chances	Cell cycle arrest	Gene expression	
Methanoic	*Caulerpa racemosa*	HL-60 (Human promyelocytic leukemia)	+	+	+		[21]
	Sargassum muticum	MCF-7 (Human breast adenocarcinoma)	+	+	+		[28]
	Enteromorpha antenna *Enteromorpha linza*	MCF-7 (Human breast cancer cell line) HepG2 (Human liver cancer cell line)	+				[29]
	Gracilaria corticata	MCF-7 (Human breast cancer cell line) HepG2 (Human liver cancer cell line)	+				[29]
	Dictyota cilliolata *Dictyota menstrualis*	HeLa (Human cervical cancer cell line)	+	+	+	Caspase 3 Caspase 9	[12]
Aqueous	*Sargassum oligocystum*	K562 (Human chronic myelogenous leukemia) Daudi (Human Burkitt lymphoma)	+				[43]
	Gracilaria corticata	Jurkat (Human lymphoblast) Molt-4 (Human lymphoblast) MCF-7 (Human breast adenocarcinoma)	+				[4,42]
	Ulva fasiata	MCF-7 (Human breast adenocarcinoma)	+				[4]
	Chaetomorpha antennina	MCF-7 (Human breast adenocarcinoma)	+				[4]
Ethanol	*Ulva fasciata*	HCT 116 (Human colon cancer)	+	+	+	Caspase 3 Caspase 9	[36]

novel Sulfated Polysaccharides (SPS), extracted from *Sargassum integerrimum* against A549 (Human lung cancer) cell line. Cell growth inhibition was resulted due to necrosis or apoptosis the treated and control cells were stained using Hoechst 33258 staining and morphological changes were observed. Comparatively, typical apoptotic cell characteristics such as cell shrinkage, cell bubbling, fragment shape nucleus and nuclear shrinkage were observed in the SPS treated cells. Flow cytometric analysis using Annexin V-FITC/PI double staining and JC-1 staining also confirms that the growth inhibition is due to apoptosis induction and further due to loss of mitochondrial membrane potential. Moreover, anti-apoptotic and pro-apoptotic protein markers expression were also tested using western blotting. According to the results, the expression level of P53; tumor suppressor protein was increased and Bcl-2; anti-apoptotic protein expression was down regulated whereas Bax; pro-apoptotic gene expression was decreased.

Several studies have found that fucoidan extracted from different seaweed species as natural bioactive compound with anticancer effect (Table 2). Fucoidan is a type of sulphated polysaccharide mainly present in brown seaweeds. There are many studies to evident the induction of apoptosis in human colon cancer cell lines such as HCT-15, WiDr, HCT116 and HT-29 by fucoidan [16,17,20]. Moreover HCT-15 cells treated with fucoidan inhibited the growth of colon cancer cell lines in dose dependent manner through apoptosis induction. The treated cells have been visualized with condensed and fragmented nucleus and Bcl-2 expression was down regulated whereas Bax, Pro-caspase 3 and 9 expressions were up regulated by the fucoidan treated cells there for it proves that this growth inhibition is due to apoptosis induction

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in the colon cancer cell lines by fucoidan [16]. Further, HCT116 and HT-29, human colon cancer cell lines treated with fucoidan (5-20 μg/ml concentrations) have also showed remarkable dose dependent and time dependent cell growth inhibition and any significant cytotoxic effect was not reported on FHC (human normal colon epithelial) cell line. This growth inhibition was also due to apoptosis induction via activation of Caspase 3, 7, 8 and 9 [20].

Table 3. Anticancer activity of bioactive compounds isolated from seaweeds

Bioactive compound	Seaweed species used to extract Fucoidan	Cancer cell type	Reference
Fucoidan	*Fucus vesiculosus*	HCT-15 (Human colon carcinoma cells)	[16]
		HT-29 (Human colon adenocarcinoma) HCT116 (Human colon adenocarcinoma)	[20]
	Sargassum sp. *Turbinaria* sp. *Padina* sp.	WiDr (Human colon adenocarcinoma) MCF-7 (Human breast adenocarcinoma)	[17]
	Sargassum oligocystum	Daudi (Burkitt lymphoma cells) K562 (Human chronic myelogenous)	[42]
	Caulerpa racemosa	HL-60 (Human promyelocytic leukemia cell line)	[21]
Laminarin	*Laminaria digitata*	HT-29 (Human colon adenocarcinoma)	[31]
Fucaxanthin	*Laminaria japonica*	EJ-1(Human bladder cancers)	[44]
	Undaria pinnatifida	HL-60 (Human promyelocytic leukemia cell line)	[15]

Laminarin is another bioacive compound present in seaweeds examined for anticancer properties. Laminarin extracted from *Laminaria digitata* has shown anticancer effects against HT-29 colon cancer cell. Laminarin showed an activity against HT-29 cell line in a dose-dependent manner. Accumulation of sub-G1 and G2-M during the flow cytometric analysis and inhibition of phosphorylation and ErbB2 expression reveals that Laminarin induces apoptosis through ErbB signaling pathway [31].

Anticancer effect of fucoxanthin extracted from *Laminaria japonica* was tested against EJ-1(Human bladder cancers) cancer cell line and observed time and dose dependent cell viability reduction. Cell morpholgical changes observed by contrastand fluorescence microscope and activetion of caspase-3 reveals that this cell viability reduction is due to apoptosis induction [44]. Fucoxanthin extracted from *Undaria pinnatifida* inhbited HL-60 (Human promyelocytic leukemia) cell line proliferation due to apoptosis induction. The results such as DNA fragmentation resuted from agarose gel electrophoresis and sandwich ELISA tests prove the activity of fucoxanthin against Leukemia cancer cell line [15].

Further, not only *in-vitro* studies but also *in-vivo* studies provide the evidance of anticancer activity of seaweeds. In this contrast, LLC (Lewis Lung Carcinoma) cells were transplanted in C57BL/6 mice and treatments (fucoidan and cyclophosphamide) were started after nine days of transplantation. it is recorded that fucoidan shows and atiancer and antimetastatic activity when the drug is used combined with cyclophosphamide [4]. Abirami & Kowsalya, 2012 [1] investigated anticancer effect of *Ulva fasciata* using albino mice (*in-vivo*). DAL (Dalton's Ascites Lymphoma) cells were transplanted in swiss albino mice and treated with methanolic extract and aqueous extracts of *Ulva fasciata* once daily for 14 days. The parameters such as hematological parameters, lipid profile, liver function tests, body weight, cancer cell counts were examined and methanolic and aqueous exracts of *Ulva fasciata* showed *in-vivo* anticancer effect against DAL cancer type. Further mammary cancer induced female rats were treated with *Eucheuma cottonii* extract (150 and 300 mg/kg of body weight) for four weeks. The tumor was reduced by E. *cottonii* extract and inhibition rate showed dose-dependent variation [27].

4. Conclusion

The therapeutic effect of seaweeds was explored due the presence of novel bioactive compounds. In this context anticancer effect of seaweed plays a major role by inducing apoptosis through intrinsic and extrinsic pathways [12,20]. Seaweed are comprised with many secondary metabolities and some of them have been isolated and further studies are reqiuired for isolation of other theraeutic compounds from seaweeds since the most of them show cytotoxic activity against cancre cells and not in normal cells. Thus further studies will open the gate to reveal new chemotherapeutic agents which are able to fight against cancers while having no or less impact on normal cells.

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ARTICLE

Moisture Absorption and Diffusion of a Carbon Composite Structure

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ABSTRACT

Composite materials are lightweight structures and have been wildly used in marine applications. A carbon composite structure usually absorbs moisture while in-service, which can significantly affect its properties, and detriments the overall performance. We perform a detailed study on moisture absorption and diffusion of a carbon fibre reinforced vinyl ester resin composite system. Composite samples are immersed directly in four different solutions at a temperature of 37±0.5 ℃ for 1444h. The moisture diffusion is analysed through the Fickian diffusion model; the diffusion parameters are subsequently determined from the gravimetric data. The moisture absorption and interaction with the composite constituents are then discussed. These indicate the fundamentals of the moisture absorption and diffusion within the carbon composite structure.

1. Introduction

Composite materials are superior in terms of specific strength, modulus and product efficiency. There are increasing interest in their applications to aerospace, automotive, medical, as well as sustainable marine structures [1]. One disadvantage is that their properties are susceptible to aggressive environments and subjected to change while in-service [2]. Moisture absorption is one of the triggering factors that can significantly affect the material performance [3].

It is known that a carbon composite structure typically absorbs moisture in a humid environment and at elevated temperatures. This has been studied by various research groups by exposing the composites in different aggressive environments, such as water, sea water, low and high temperatures, and coupled with different loads [3-6]. The reinforcements include nature fibres, such as hemp fibre [7], jute fibre [8], sugar palm fibre [9], bamboo cellulose fibre [10], as well as synthetic fibres, e.g. graphite fibre [11], glass fibre [12,13], carbon fibre [14,15], and hybrid braided fibres [16]. Among these, the commonly used matrices are epoxy resins and unsaturated polyester resins. Vinyl ester resin (VER) is a bisphenol-d rived polymer, which offers better resistance to moisture absorption and hydrolytic attack than polyester [17]; carbon fiber (CF) has a high degree of corrosion resist compatibility [2]. Thus, carbon fibre reinforced vinyl ester resin (CF/VER) composite has great potential in sustainable marine structures.

In this paper, we studied the fundamentals of moisture absorption and diffusion in a CF/VER composite system. Section 2 introduces the principles of the Fickian diffusion model; Section 3 shows the detailed experimental

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procedures; Section 4 presents the results and discussion; and Section 5 concludes the study.

2. Fickian Diffusion Model

Generally, moisture absorption and diffusion of a polymer-matrix composite can be described by Fick's second law of diffusion [18,19], where the moisture content initially increases linearly with the square root of time and then gradually slows down until it reaches the effective moisture equilibrium, see Figure 1. For a material that follows the Fick's law as in Eqn 1 is also named as a single-phase Fickian material.

$$\frac{\partial c}{\partial t} = D_z \frac{\partial^2 c}{\partial z^2} \quad (1)$$

where: c is the specimen moisture concentration, g/mm^3;

t is time, s;

$\frac{\partial c}{\partial t}$ is time rate of change in moisture concentration, g/(mm^3·s);

D_z is Fickian moisture diffusivity constant, mm^2/s;

z is through-the-thickness direction, mm.

The single-phase Fickian diffusion model as shown in Figure 1 can be established using Eqns 2-9 [20]. To predict the moisture content, the equilibrium content M_m and the Fickian moisture diffusivity constant D_z are essential [21,22]. They both can be calculated from gravimetric data, and follow:

$$D_z = \pi[h/(4M_m)]^2\left[(M_y - M_x)/(\sqrt{t_y} - \sqrt{t_x})\right]^2 \quad (2)$$

where: h is the thickness of the specimens, mm;

M_m is the equilibrium moisture content of the specimens, %;

M_x, M_y is the moisture content of any time interval t_x, t_y in the linear portion of the curve M_i versus $t^{1/2}$, %.

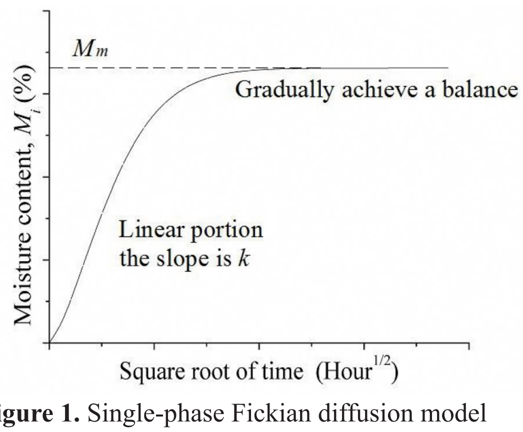

Figure 1. Single-phase Fickian diffusion model

Moisture absorption rate, k, is the slope of the linear part of the curve:

$$k = (M_y - M_x)/(\sqrt{t_y} - \sqrt{t_x}) \quad (3)$$

Thereby:

$$D_z = \pi[kh/(4M_m)]^2 \quad (4)$$

The moisture content in a material at a given moisture exposure level is:

$$M(T,t) = M_b + G(M_m - M_b) \quad (5)$$

where: T is temperature, °C;

$M(T,t)$ is moisture content as a function of time and temperature, %;

M_b is baseline moisture content, %;

M_m is moisture equilibrium content, %;

h is thickness of material, mm;

G is moisture absorption function and follows:

$$G = 1 - \frac{8}{\pi^2}\sum_{j=0}^{\infty}\frac{\exp\left[-(2j+1)^2\pi^2\left(\frac{D_z t}{h^2}\right)\right]}{(2j+1)^2} \quad (6)$$

Approximately:

$$G = 1 - \exp\left[-7.3\left(\frac{D_z t}{h^2}\right)^{0.75}\right] \quad (7)$$

To reach a given moisture content at a fixed temperature and moisture exposure level, the time can be predicted as follows:

$$t = \frac{h^2}{D_z}\left[\frac{-1}{7.3}\ln\left(1 - \frac{M(t) - M_b}{M_m - M_b}\right)\right]^{4/3} \quad (8)$$

Regardless the ambient moisture exposure level, the time necessary for a completely oven-dried specimen to get 99.9% of moisture equilibrium at a given temperature is:

$$t_{\max}(T) = \frac{0.93h^2}{D_z} \quad (9)$$

3. Experimental

3.1 Sample Preparation

The matrix used in this research is vinyl ester resin and its chemical structure is shown in Figure 2; the reinforcement is carbon fibre T300-1K purchased from TORAY, Japan.

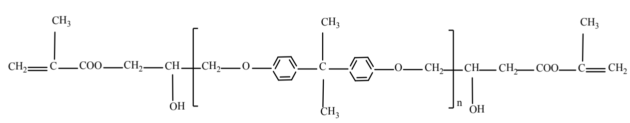

Figure 2. Chemical structure of the vinyl eater resin used in this research

To produce a composite sample, resin, hardener and crosslinker were thoroughly mixed at room temperature,

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the carbon fibre was then put into the mixture to ensure sufficient impregnation. The impregnated fibres were placed following $[0°/+45°/-45°/90°]_s$, and locked inside a mould. The whole mould was then subjected to a curing process of 90 ℃ /2h+110 ℃ /2h+130 ℃ /2h+150 ℃ /2h. After mould releasing, the composite specimens were cut into designated sizes and subjected to aseptic processing as detailed below.

The specimens were rinsed in distilled water under ultrasonic cleaning for 15 minutes. The naturally dried samples were exposed to ultraviolet (UV) light for 30 min, and scrubbed with anhydrous ethanol; then oven-dried and weighted separately as W_0, which was used as reference for water absorption experimenting, using an electronic balance with an accuracy of 0.1mg. The specimens were then stored in sterilized jars ready for testing.

3.2 Moisture Absorption and Degradation

The moisture absorption and degradation studies were carried out in four solutions with different pH: (i) distilled water (DTW); (ii) hydrogen peroxide solution (HPS); (iii) Fenton's reagent (FTR); (iv) phosphate buffered saline (PBS). The DTW was prepared following ISO 3696 and GB/T 16886.13; HPS was prepared using 3% H_2O_2 (in volume fraction) from LIRCON, Shandong, China; FTR contained 100 μmol/L $FeSO_4$ and 3% H_2O_2 (in volume fraction); PBS was prepared from distilled water and contains: NaCl 140 mmol/L, Na_2HPO_4 8.1 mmol/L, KH_2PO_4 1.5 mmol/L, and KCl 3 mmol/L.

Experimental procedure follows below: firstly, solutions were stored in different sterilised jars with previously processed composite samples. Here, the volume ratio of the specimens and the test solution is at least 1:10 (GB/T 16886.13), and the specimens must be completely immersed in the liquid. The jars were then placed into a constant temperature water bath which had previously reached the specified steady-state of 37±0.5℃ , and the water level must be higher than that in the jars.

After the designated period, each specimen was taken out and rinsed with distilled water for at least three times, surface moistures were wiped out entirely with dry and clean filter paper. The specimen was weighed immediately to the required precision and recorded as W_i, along with total elapsed time and the time interval since previous measuring, then put the sample back into the jar. Each sample should not be out of the jar for more than 5 min per reading (ASTM D5229). The sample weight was monitored until effective moisture equilibrium was reached. Since H_2O_2 in HPS and FTR would become invalid after a certain time, both solutions were changed every week.

The moisture content (M_i) of specimens at different time intervals could be calculated by the weight difference from Eqn 10:

$$M_i = \frac{W_i - W_0}{W_0} \times 100\% \tag{10}$$

After been immersed in different solutions for 1444 h (two months), one specimen from each solution was cleaned following the same procedures as above, and then oven-dried until it reached the specified dry steady-state. The oven-dried weight was recorded as W_d, and the weight change (M_c) is calculated using:

$$M_c = \left| \frac{W_0 - W_d}{W_0} \right| \times 100\% \tag{11}$$

The value of pH in each solution was also monitored using a precision pH meter every week; surfaces of the immersed composite specimens were also examined using a scanning electron microscope (SEM) SU-1500 produced by HITACHI to detect any interfacial debonding.

4. Results and Discussion

4.1 Fickian Diffusion

The moisture content M_i versus the square root of time $\sqrt{t}$ is plotted together with the Fickian diffusion model in Figure 3. It is clear that the experimental data well fits the Fickian model except the one in FTR. This is because FTR has stronger oxidation effect for its well-known classical reaction between Fe^{2+} and H_2O_2 [23] than the other three mediums. The composite sample undergoes severe corrosion during the same time interval, causing more gaps and voids inside the specimens, which in turn leads to heavier moisture absorption.

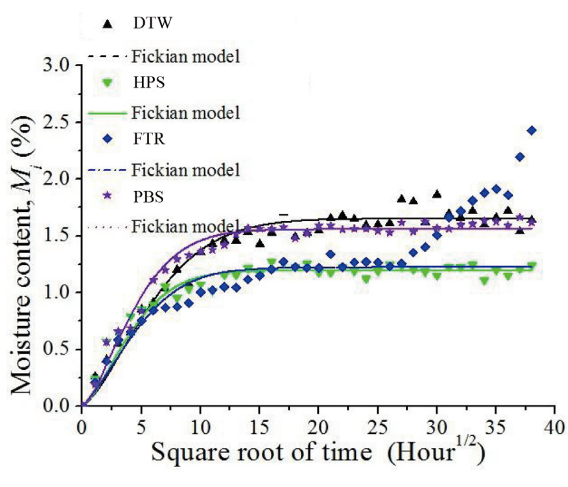

Figure 3. Moisture absorption and diffusion curve of composite specimens, curves are fitted by using the Fickian model

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Three parameters of moisture absorption were computed from gravimetric data using Eqns 3, 4, and 10, resulting data are shown in Table 1. The value of D_z in TDW is the lowest, which indicts that the moisture diffusion is the slowest. This attributes to the lowest osmotic pressure in pure water which can accelerate the diffusion of moisture compared to the other three solutions. The value of M_m in both HPS and FTR are relatively low, which is caused by the corrosion of the specimens as seen from the SEM micrographs in Section 4.4.

Table 1. Parameters of moisture absorption in different solutions

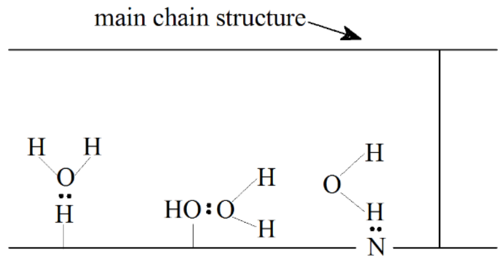
Coefficients	Solutions			
	TDW	HPS	FTR	PBS
M_m (%)	1.65	1.20	1.23	1.59
k ($s^{-1/2}$)	2.46×10^{-5}	2.50×10^{-5}	2.32×10^{-5}	3.05×10^{-5}
D_z (mm^2/s)	3.91×10^{-6}	7.69×10^{-6}	6.34×10^{-6}	6.49×10^{-6}
t_{max}(37℃) (h)	594.60	302.29	366.65	238.76
$\sqrt{t_{max}(37℃)}$ ($h^{1/2}$)	24.38	17.39	19.15	15.45

The time when M_i reached 99.9% of its moisture equilibrium is determined from Eqn 9, and shown in Table 1. The predictions show good agreement with experiments shown in Figure 3. Therefore, it is concluded that the single-phase Fickian diffusion model can properly predict the moisture diffusion of the CF/VER composite.

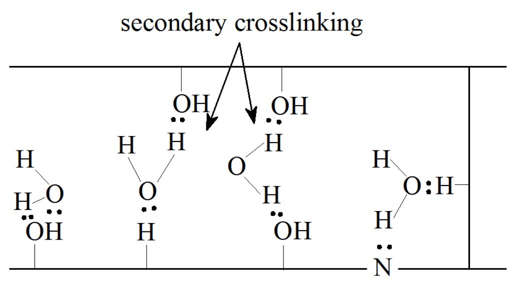
4.2 Moisture Absorption and Interaction

When composite specimens are immersed in a liquid medium, there are two main actions between water molecules and composite microstructures: (1) physical diffusion; (2) chemical degradation.

Physically, the moisture absorption of composite is mainly the diffusion of water molecules. Water go through the defects in the matrix and interface such as holes, cracks to penetrate into the composite at first. This leads to the swelling of matrix and molecular chain relaxations, causing changes in residual stresses within the composite which may further result in the formation of micro-cracks [24]. All these can speed up the moisture absorptions. In a polymer matrix, there is a distribution of micro-porous at molecular level, and water molecules can easily get into the internal of cross-linked resin. These absorptions can destruct the hydrogen bonds between original macromolecular chains, weaken the cross-linking strength and decrease the wear resistances. Thus, the existence of micro-porous facilitates the convection which also accelerates the absorption of water. The water molecules continue to spread into the composite interfaces, and initiate serious effects such as further swelling of the matrix and the generation of internal stresses. These can cause significant damage such as interface debonding and delamination, crack propagation, and so on, further increase the moisture content within a composite. Meanwhile, carbon fibre is a hydrophilic material, water molecules can easily form hydrogen bonds with the carbon fibre. Thereby, they undermine the combinations of the fibre and matrix, which decreases the interfacial strength and gradually lead to the failure of the interfaces. Furthermore, the dissolution and penetration of water soluble substances can generate the osmotic pressure within the composite which also can accelerate the diffusion of water molecules.



(a) Formation of hydrogen bonds



(b) Formation of secondary crosslinking

Figure 4. Model of potential secondary crosslinking between water molecules and a polymeric matrix material

The chemical degradation effect is mainly through the chemical reactions between water molecules interior the composite and some elements within the matrix. Water molecules connect with macromolecular chains can react with the hydrophilic groups to undermine the original composition of the composite, further lead to the irreversible changes in material properties. Thus, if there are chemical groups such as ester which can easily degraded under the action of water molecules, the material would lose weight in the humid environment. Also, water molecules are polar molecules, which may be combined with hydrophilic groups within the matrix or fibres to form hydrogen bonds or other new bonds, or even lead to secondary cross-linking between molecular chains. Zhou and Lucas [25] established a model to describe this new bonding between water and epoxy network as illustrated in Figure 4, which has similarity with the moisture absorption within our CF/VER composite structure.

4.3 Degradation Analysis

The varieties of pH over two months are plotted in Figure 5. There is a rapid change of pH in the TDW in the first week, and then becomes stabilised. The pH varieties are all very small in other three solutions, and there is almost the same trend of pH between HPS and FTR. The overall changes of pH in different solutions are shown in Table 2, with a maximum value of 1.42. It is noted that the secure pH value change for medical material leaching solution is no more than 1.5 [26], thus the CF/VER composite can be preliminarily determined to be safe.

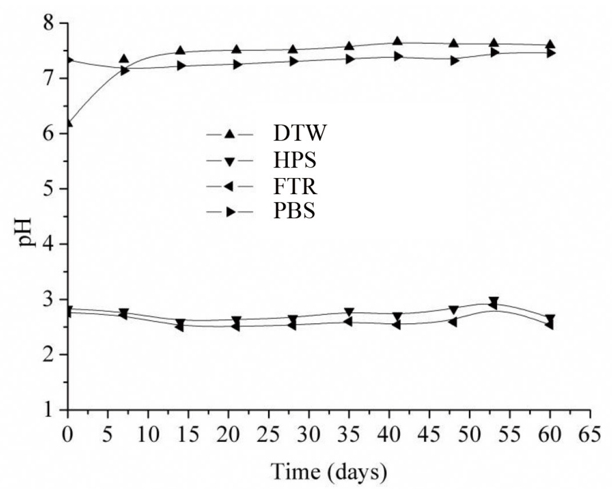


Figure 5. The value of pH in different solutions over two months

Table 2. The changes of pH in different solutions in two months

The value of pH	TDW	HPS	FTR	PBS
minimum	6.18	2.59	2.50	7.14
maximum	7.60	2.99	2.90	7.47
changed	1.42	0.40	0.40	0.33

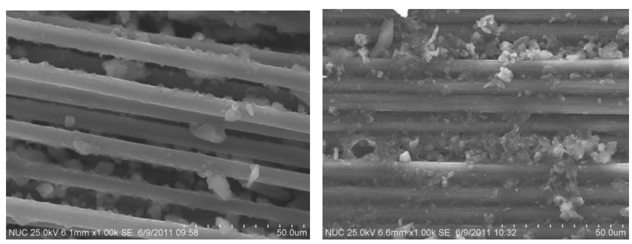
The weight changes after immersed for 1444 h (i.e. two months) are determined from Eqn 11 and show in Table 3. The M_c has increased by 0.35% in pure water, indicating that water molecules are combined with hydrophilic groups to form the hydrogen bonds, or the secondary crosslinking occurred between molecular chains as discussed in Section 4.2. For HPS and FTR, the composite samples loss weight giving negative M_c, and FTR has the strongest corrosive effect to the CF/VER composite. The weight of the specimens that immersed in PBS are almost unchanged.

Table 3. Weight changes after immersed in different solutions for 1444 h

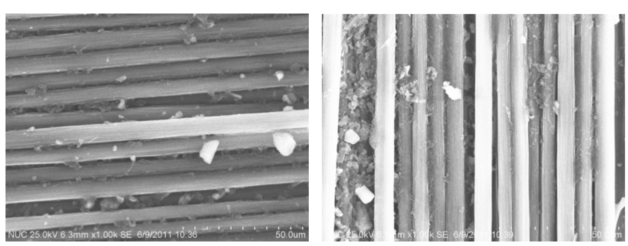
	TDW	HPS	FTR	PBS
M_c (%)	+0.35%	— 0.61%	— 2.69%	+0.03%

4.4 Surface Debonding

Micrographics of the composite sample surfaces before and after immersed in different solutions are shown in Figure 6. As it can be seen from the original composite, the adhesion of the matrix and fibres are good, fibres were tightly wrapped by the matrix. After immersed for five weeks, the composite interface remains to be good in TDW and PBS, which indicates that the degradation of CF/VER composite in such solutions are very small. This correlates with the few changes of pH as in Figure 5. However, corrosions of composite interfaces in HPS and FTR are quite obvious, leaving smooth fibre surfaces exposed to the acidic solutions, which is detrimental to the composite properties.



(a) Original sample (b) in TDW bath



(c) in HPS bath (d) in FTR bath

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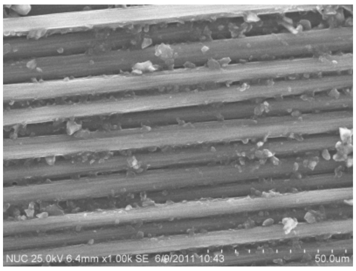

(e) in PBS bath

Figure 6. SEM micrographs of composite samples before and after immersed in different solutions for five weeks

5. Conclusions

We performed detailed experimental and analytical studies on moisture absorption and diffusion of a carbon fibre reinforced vinyl ester resin composite system. Composite samples were immersed in four different solutions at a temperature of 37±0.5 ℃ for 1444h. Moisture absorption curves of CF/VER composite in different solutions are obtained and the diffusion processes basically follow the single-phase Fickian diffusion model. The diffusion coefficients are then determined from the gravimetric data. The moisture diffusion in pure water is the lowest due to its low osmotic pressure; the changes in pH falls within a safe rang; and CF/VER system has very good corrosion resistance in salted water. These infer the fundamentals of the moisture diffusion within the carbon composite structures, and facilitate their applications in marine engineering.

Declaration of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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ARTICLE

Zoning Marine Disposal for Dredged Material Management: A Case Study in Vietnam

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ABSTRACT

The fast growth of Hai Phong ports in the two last decades requires not only their upgrading facilities but also expanding port area and dredging their shipping channels (existing and new ones) that generate a huge amount of unused dredged materials. While all existing dumping sites in sea waters and on land get over capacity, looking for new dumping sites in sea waters is an urgent need. This study is to zone coastal waters of Hai Phong for suitable dumping sites meeting sustainable coastal management. Multi-criteria overlay analysis on GIS platform was employed with the criteria of natural conditions, environment and socio-economics for zoning coastal waters of Hai Phong. These criteria were detailed into eight sub-criteria and then developed to eight GIS weighted thematic sub-layers of bottom depth, litho-hydrodynamics, ecosystems, distribution of benthos, distance to residential areas and tourist sites, distance to aquaculture area, distance to ecosystems and distance to conservation areas. Analysis results show the highly suitable zone for dredged material dumping in South, South West Hai Phong at depth below 15m to the deeper areas. Disposals of dredged materials in the zone would minimize impacts on the environment, ecology and socio-economics in surrounding waters and coastal areas.

1. Introduction

Shipping channel material dredging that is vital to many harbors worldwide to maintain their operation normally generates some amount of dredged materials. These materials disposed on mainland, islands or in open waters can make not only benefits (reuse, recycle, etc.) to socio-economic development [13] but also negative impacts on the environment [5,13,16]. For many years, environmental impacts of dredged material disposal sites, particularly in marine waters have been studied and assessed for all environmental components as sediment, water and biological issues [1,4,9]. To mitigate environmental impacts of dumping in sea waters, London Convention 1972 (Annex III) issued eight general criteria on characteristics of dumping sites, dumped materials and potentially impacted ecosystems to determine dumping area and sites. Following these general criteria, some nations have developed their adapted criteria. For example, the United States in 1992 issued Ocean Dumping

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Act with detail regulations on management, dumping materials and conditions, and criteria for disposal sites [2]. Australia [14] and Ireland issued Sea Dumping Acts with their specific criteria for dumping sites . Vietnam recently mentioned a marine dumping regulation in the Law on Resources and Environment of Seas and Islands.

Hai Phong sea ports designed by the Government of Vietnam as the main gate and taking an important role for socio-economic development in North Vietnam are located close to the high ecological conservation areas of Cat Ba Biosphere Reserve listed by MAB (Man and the Biosphere)/UNESCO (2004) and Ha Long Bay Natural Heritage recognized by UNESCO (1994), and next to the famous touristic area of Do Son that remarkably contributes to economic growth of Hai Phong. The channels of Hai Phong sea ports are also considered as the main route for the development of the maritime industry in North Vietnam. However, these channels are in sedimentation and dredged every year. According to the Northern Maritime Safety Corporation of Vietnam, the needs of sandy and muddy dredging annually to maintain the channels are up to 2.5-3 million tons with minimum cost estimated around 40-50 billion VND (Vietnamese currency). Recently, Hai Phong sea ports have been expanded seaward with the construction of a new harbor namely Lach Huyen International Gateway Port that will be able to receive ships of 100,000 DWT (dead weight tonnage). It is obvious that the development of Hai Phong ports needs to dredge a huge amount of sediments for construction stage and shipping channel maintenance annually. However, a serious raising problem is where to dispose the dredged materials, while all selected sites inland and in coastal areas are in over capacity. To tackle the problem, some sites in offshore waters were proposed but minimal environmental impacts when disposal of dredged materials, especially on the areas of high ecological values as Cat Ba Biosphere Reserve and Ha Long Bay Heritage. This study is based on multiple criteria overlay analysis using geographic information system (GIS) to zone areas suitable for disposing dredged materials to meet the goal of sustainable management of sea port area.

2. Materials and Methods

2.1 Study Area

The study area is in Hai Phong coastal zone bordering with the districts of Hai An, Do Son and Kien Thuy in the North, Cat Hai district (with Cat Ba Biosphere Reserve and close to Ha Long Bay Natural Heritage) in the East, the Gulf of Tonkin in the South and the West. There are six large rivers discharging in the study area (Figure 1), being strongly influenced by the rainy season and dominated by tide with the highest amplitude over 4m. Seabed is fairly flat with a depth up to 30m. The area is affected by waves with their height of 0.5 to 0.9m average, reaching a maximum of 5.6m and the direction changes seasonally. Surface sediments on sea bottom are mainly small grey-brown and greenish-grey silt [15].

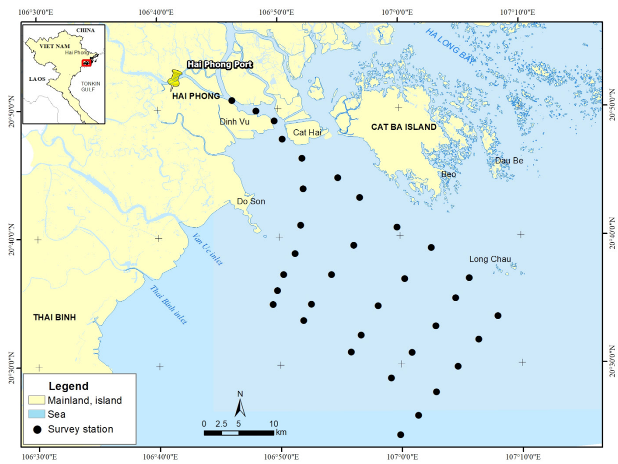

Figure 1. Study area and survey stations

Source: Project DT.MT.2015.721

Surrounding the study area, the ports and maritime activities of Hai Phong have been developed in Bach Dang and Cam estuaries and recently expanded seaward to construct new international port of Lach Huyen associated with the economic zone of Dinh Vu - Cat Hai. The total goods throughput of Hai Phong ports was increased by 25 times for 32 years, 50.1 million tons in 2012 compared to 2 million tons in 1980. From 2000 to 2013, the number of ships entering the port increased by 1.5 times. The growth rate of goods through the ports reached 15-20% per year. As such, the amount of dredged materials in Hai Phong seaport area also ranged from 650 m^3 to 2000 m^3 (2011-2016) (Table 1).

Hai Phong shipping channel system includes 8 sections of total 91.4km long with four main channels of 43km (Lach Huyen, Ha Nam, Bach Dang, Song Cam). All the channels have been in heavy sedimentation. In addition to economic concerning activities, Do Son marine tourist area visited by millions tourists annually is located in the Northwest. Marine fishing that greatly contributes to the Hai Phong gross domestic production takes place in three major fishing grounds as Cat Ba, coastal Thai Binh estuary to Quang Ninh and offshore Long Chau - Ba Lat [7]. Aquaculture with large potential areas stretches from Cat Hai, Tien Lang, Kien Thuy, Do Son, Duong Kinh

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Table 1. The mass of sediment dredging for maintenance and construction of seaport channels in Hai Phong during 2011-2016

The mass	2011	2012	2013	2014	**2015**	**2016**
Dredging for maintenance and construction of jetties (m^3)	840.000	645.000	875.500	797.320	798.800	300.700
Dredging for maintenance of Hai Phong channels (m^3)	985.884	1.262.000	679.984	1.022.299	1.112.419	119.699
Dredging for maintenance of Pha Rung channel (m^3)	164.634	99.727	51.849	57.297	60.104	221.561
Total (m^3)	1.990.518	2.006.727	1.607.333	1.876.916	1.971.323	641.960

Source: Project ĐT.MT.2015.721

and Hai An. Over the past ten years, the area of brackish aquaculture ponds annually has expanded slightly, while the area of marine culture, including intertidal culture (clams, etc.) and cage culture tends to highly increase, especially in Cat Hai district.

In East and Southeast study area is the Cat Ba island conservation with Cat Ba National Park and Cat Ba Biosphere Reserve including four marine ecosystems of mangroves, tidal flats, corals, and soft bottom. In which, coral ecosystem with a total of 177 species is limitedly distributed in Southeast Cat Ba islands and Long Chau islands, relatively far from the area with marine activity. Mangrove ecosystems with a total of 31 species, spread out nearly 18 thousand hectares, mainly in the coastal communes of Phu Long, Cat Hai, Bang La and the river mouths of Bach Dang, Cam, Lach Tray, Van Uc, Thai Binh. It is quite diverse in species of the ecosystem [15]. Tidal flat ecosystem is spatially distributed along the coast of the islands and tidal zones from Cat Ba to Thai Binh estuary. It is diverse in species but distributed uneven and highly dependent on bottom materials (sand, gravel, reef and mud, sandy mud) [15]. Of the ecosystem, benthic communities with 340 species belonging to 186 genera, 84 families have been recorded. The ecosystem of soft bottom (including water mass) is largest but less biologically diverse than others. About 400 species and subspecies of phytoplankton, 131 species of zooplankton, 196 species of marine fish have been found. The bio-diversity index (H') of the soft bottom ecosystem ranged from 0 (zero) to 2.72, averaging 1.72, indicating a low bio-diversity in the area.

2.2 Materials

Data on natural condition, marine environment and ecosystems were mainly resulted from the Hai Phong city-level project "Study on scientific basics for planning dredged material disposal sites in the Hai Phong coastal area" coded DT-MT.2015.721 in the period 2015-2017 and the VAST project coded KHCBBI.01/18-20 implemented in 2018-2020. GIS layers on natural condition were referred to the simulation outcomes using litho-hydrodynamic numerical modeling recently [17].

Socio- economic data and documents were collected from statistic books of Hai Phong city, socio-economic annual reports of the city (including land use maps) and the project reports of Lach Huyen International Gateway Port. Besides, data and information were also contributed by interviews of relevant agencies as Hai Phong Maritime Administration, Hai Phong Department of Natural Resources and Environment, local authorities of coastal and island districts.

2.3 Methods

Zoning dredged material disposal to minimize environmental impacts for port and maritime sustainable management will follow the approach of sustainable development.

In overall, multi-criteria overlay analysis (MCOA) on GIS platform (ARCGIS 10.1) is the main method to employ to zone disposing dredged materials from ports and shipping channels in Hai Phong. To do this MCOA, a database of a 1/50,000 base map and GIS layers of natural condition, environment and ecosystem, and socio-economics was established based on data collected from the projects and other books, reports. After making the layers in GIS platform, they were assigned with weights aggregated from Delphi analysis and then overlaid to get results of zoning maps (Figure 2).

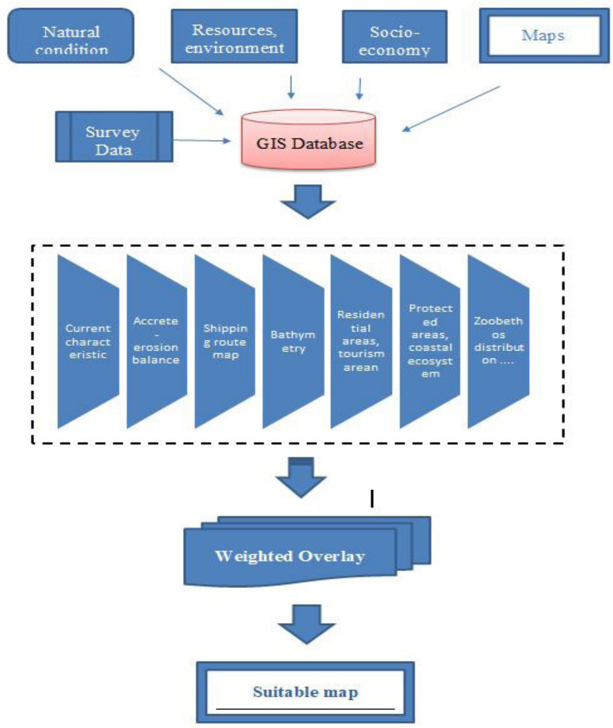

Figure 2. Multi-criteria GIS overlay analysis for zoning marine area of dredged material disposal

Note:
Data on environmental and ecological characteristics was collected in sampling and observing stations at three layers (surface, middle and bottom) of water columns covering the whole study area (Figure 1) for two seasons (dry and rainy) in 2015-2017 and 2018-2019 supplementation. Sampling and analyzing environmental and ecological parameters followed the methods issued in the National Regulations of the Ministry of Natural Resources and Environment of Vietnam (MONRE) [10],[11]. Data on the characteristics of marine and coastal ecosystems were gathered via surveys employing published professional methods [8]. Relevant data on socio- economics were selected from related year books and reports and put in sheets of Microsoft Office Excel 2007. After that, collected data were managed in the GIS database.

Development of criteria: following three poles (social, economic and environmental) of sustainable development approach, three relevant criteria (environmental, social and economic) were established. Based on its characteristics, each was detailed into sub-criteria with specific values. The values were determined by reference to some similar studies and the analysis of relevant current status characteristics of the study area done by the projects DT-MT.2015.721 and KHCBBI.01/18-20.

Making GIS layers and weight assignment: based on 1/50,000 base map of the study area, collected data divided into three groups of environment (including natural condition and ecological features) and socio-economics were input in GIS software to produce thematic normalized layers. Data on the environment were used in GIS platform to develop spatial thematic layers, including: litho-hydrodynamic layers (currents and accretion-erosion) that were referred to previous study[17] , bathymetry layer, layers of protected areas and coastal ecosystems, and benthic distribution layers. Data on socio-economics were employed for developing spatial thematic layers on shipping channels, residential areas and tourist sites. Each GIS thematic layer was attributed with sub-criterion values.

To assign weights to the layers and their criteria and attributes (weight assignment as follows: 1- low, 2- medium, 3- high), the Delphi method [6] was applied with 35 expert respondents. The weight was determined through a comparative evaluation of attribute pairs of the relevant factors regarding the likelihood suitability of pixels. The evaluation process of weight determination was performed according to Saaty matrix [12]. The importance of input layers and their attributes was determined by applying a 9-point Saaty pair matrix.

Spatial analysis for zoning of disposal areas: multi-criteria analytical GIS overlay was the integration of the normalized layers on the suitability levels for dredging materials and weighted overlaying. The overlaying model (Figure 2) resulted in a new layer showing the suitability for disposing with suitable values in the range 0-1. The zone with values close to 1 (one) would meet all conditions of natural characteristics, socio-economics and environment and ecology, being the most suitable for minimal impact dumping dredged materials, and vice versa, the zones with values closer to 0 (zero) would not match.

3. Results and Discussions

3.1 Potential Environment Impacts of Disposing Dredged Materials in Hai Phong Port Waters

On environmental quality of Hai Phong port area, all monitoring parameters of front waters required by the Government of Vietnam have met national technical regulations although in some ports, water has been locally polluted by oil (according to the project DT-MT.2015.721).

Dredged material dumping in the coastal waters of Hai Phong ports would have potentially environmental and ecological impacts. One of the obvious and foreseeable direct impacts is the impact on the benthic fauna at the dumping sites, changing or destroying the benthic fauna and flora at the sites, although in this area the benthic

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fauna and flora are quite poor. The impacts on water and sediment environment quality and socio-economics are also difficult to avoid. These key impacts are summarized as follows.

Impacts of increasing water turbidity at disposal sites and surrounding areas: when dumping dredged materials (composed of over 80% muddy clay according to the project DT-MT.2015.721) marine water at the sites and surrounding areas will be increasingly turbid. The increasing of water turbidity potentially impacts on benthos at the sites and adjacent ecosystems, tourist beaches, aquaculture and nursery grounds, fisheries. Besides, the dumping for years can have cumulative environment impacts of sedimentary pollutants that meet at present national technical regulations.

Impacts of dumping dredged materials on socio-economics are much related to increasing cost of material transport from dredging sites to disposal sites. To minimize the impacts on valuable ecosystems in the conservation areas of Cat Ba Biosphere Reserve and Ha Long Bay Natural Heritage, the dumping zones and sites must be far enough from the dredging sites. This makes transport cost increased (cost of VND 8,424 for 1 cubic meter of dredged materials per 1 km maritime transport according to Hai Phong People Committee Decision). Besides, increasing shipping density in shipping channels in the port areas will make the increase of maritime incidents.

3.2 Development of Criteria

Three criteria were identified according to the principles of sustainable use of natural resources and environmental protection, including economic, environmental and social criteria. The combination of economics and society generated a socio-economic criteria. These criteria were developed and then consulted with experts, scientists, managers, within the framework of the project DT.MT.2015.721 and KHCBBI.01/18-20 (Table 2).

3.2.1 Environmental Criteria

To develop the criteria, the following basic issues were taken into account: natural condition (two first criteria), environmental issues and ecological features:

Criterion of seafloor topography (bathymetry): the dumping area should be located in a region stable, minor affected by currents and waves, and no sedimentation. This was to prevent dumping materials from diffusing back the water environment.

Criterion of litho-hydrodynamics: this included the parameters of currents, waves, sediment transportation and changes in bottom topography. Changes in bottom topography is normally resulted from litho-hydrodynamic conditions of the area [17]. These results showed that the suitable dumping site was placed with the smallest topographic changes under all meteorological conditions, including monsoons and typhoons. The hydrodynamic criteria were quantified digitally as an input to the GIS multi-criteria overlay analysis.

Criterion of dispersing suspended sediment: for suspended matter from the dumping sites not affecting the sensitive areas of ecology and socio-economics of Hai Phong as Cat Ba islands, Long Chau islands, Do Son beaches, the dumping sites should be located in the zones as far as possible from those islands and beaches. However, this criterion was difficult to be quantitative. As such, a numerical model simulation on the influence of suspended matter to the surrounding sea was referred [17].

Criteria of distances to marine ecosystems and marine conservation areas (corals, sea grass, mangroves and other tidal wetlands): the simulation results of suspended matter dispersion [17] and some works [3] indicated that the ecosystems, marine conservation areas could be impacted by dredged materials at the dumping sites within 5km distance. Therefore, dumping in the zones in a distance of 5-10km (and farther) from the ecosystems and the conservation areas was relatively safe.

Criterion of benthic distribution: a biodiversity index (H’) was used to set up a criterion for benthic distribution. Based on the classification of bio-diversity index for environmental quality, the areas with H’<1 (less biodiversity) indicating bad environment were suitable for dredged material dumping (not much impacting on benthos and the environment). The areas with H’ ranged from 1-3 were relatively suitable for the dumping. Whereas, the areas with H’ greater than 3 were not suitable for dumping.

Criteria for distribution of fishing grounds and nursery grounds: fishing and nursery grounds are negatively impacted by pollutant dispersion in sea water. In the area, pollutants from dredged materials could seriously impact on the grounds within a distance of less than or equal to 5km from the dumping zones [17]. Therefore, a distance of 5-10 km and the farther could be relevant to dumping areas.

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Table 2. Combination of criteria system used for determining the suitable dumping sites

Criteria	Sub-criteria	Attributes	Data sources
Natural condition and Environment	Bottom depth	<6m	Topographic map, nautical chart (base maps)
		6-20m	
		20-30m	
		>30m	
	Litho-hydro dynamics	Erosion	Numerical model [11]
		Sedimentation	
	Marine ecosystems (corals, sea grasses, mangroves, beaches, tidal flats, underwater soft bottom)	<5,000m	Project research results
		5,000-10,000m	
		>10,000m	
	Distribution of benthos	H’<1	Project research results
		1<H’<3	
		H’>3	
Socio-Economics	Distance to residential areas, touristic sites (beaches)	<5,000m	Administrative maps (base maps)
		5,000-10,000m	
		>10,000m	
	Distance to shipping channels	<5,000m	Nautical charts (base maps)
		5,000-10,000m	
		>10,000m	
	Distance to aquaculture area	<5,000m	Land use maps
		5,000-10,000m	
		>10,000m	
	Distance to conservation areas, underwater planned structures and facilities	<5,000m	Land use maps
		5,000-10,000m	
		>10,000m	

Source: project ĐT.MT.2015.721

3.2.2 Social-economic criteria

To minimize the impacts of dredged material disposal on the city socio-economic development, the dumping area should be: (1) far away from residential areas and coastal tourist areas; (2) not on areas to be planned for underwater structures such as optical fiber systems, electrical cables, power lines, gas pipes, sewage pipes; (3) certain safe distance from the shipping channels to prevent dredged materials from their re-settlement on the channels.

Criterion of coastal residential areas: residential areas would be directly affected by dumping and the most concern when conducting any socio-economic development activity. The environmental impacts of dredged material dumping must be minimum in these areas. This means dumping areas should be as far as possible. A distance of at least 10km [3] was taken for the criterion.

Tourist beach criterion: beaches in tourism use include Do Son, Cat Co 1, 2, 3, Cat Dua, Van Boi and Tung Thu (Cat Ba islands). The environmental impacts of the dredging materials from dumping areas on beaches must be minimal. This means dumping areas should be as far as possible. A distance of at least 10km [3] was taken for the criterion.

Criterion of aquaculture area: dredged material dumping might negatively impact on aquaculture area adjacent to disposal sites, decreasing aquaculture productivity and yield. A distance of 5km and farther from the disposal sites [17] should be kept.

Criteria of socio-economic development planning (underwater planned structures and facilities): the dumping area cannot be in an area that already exists or is planned for underground infrastructure such as fiber optic cable, electric cable, gas pipeline, wastewater pipe ... In terms of economics, the distance from dumping area to dredging site is a major concern. Disposal sites closed to dredging areas are more convenient and economical for dredged material transportation. Furthermore, the transport of dredged materials to dumping sites will generate more emissions, noises and busier shipping. Therefore, it is not only of saving the cost of transporting but also of environmental protection and maritime safety. According to the project DT.MT.2015.721 and other works [3], the suitable distance of 10km from the dumping site should be taken into account.

3.3 Zoning Dredged Material Disposal to Minimize Environmental Impacts

3.3.1 Weight Assignment

Weight assignment was made for criteria, sub-criteria and their attributes. The 9-point pair matrix resulted in the values of the criteria, sub-criteria and attributes (Tables 3,4,5).

Table 3. Importance of criteria in dumping site selection

No.	Criteria	Weight
1	Natural condition	0.36
2	Environment	0.33
3	Socio-economics	0.31

Table 3 presents three key criteria that were weighted in the total weight being 1 (one). Among the three criteria, the criteria of natural condition was most important, followed by the environmental criteria and the socio-economic criteria. Weighting detail criteria (sub-criteria) was done in the same way as for the three key criteria. Of the natural condition, the sub-criterion of litho-hydrodynamic was more important than the remain one. Similarly, the sub-criterion of ecosystems and the

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distance to conservation area were more weighted than others (Table 4). The weights of attributes (Table 5) show the more importance of farther distances from impacted objects (shipping channels, aquaculture areas, conservation areas, residential areas, etc.). For benthos, the bottom area with H' less than 1 was the most suitable for dumping.

Table 4. The weights of the sub-criteria

Criteria	Sub-criteria	Weight
Natural condition	Bottom depth (m)	0.4
	Litho-hydrodynamics	0,6
Environment	Ecosystems	0.65
	Distribution of benthos	0.35
Socio-economics	Distance to conservation areas (m)	0.39
	Distance to residential areas, touristic spots (m)	0.30
	Distance to shipping channels (m)	0.15
	Distance to aquaculture area (m)	0.16

Table 5. The weights of the attributes of each sub-criterion

Sub-criteria	Attributes	Weight
Bottom depth	<6m	0.0445
	6 - < 20m	0.1034
	20 - < 30m	0.2646
	≥30m	0.5874
Litho-hydrodynamics	Accretion	0.9000
	Erosion	0.1000
Distance to residential areas, tourist sites	<5,000m	0.0581
	5,000-10,000m	0.2067
	>10,000m	0.7352
Distance to shipping channels	<5,000m	0.0581
	5,000-10,000m	0.2067
	>10,000m	0.7352
Distance to aquaculture area	<5,000m	0.0581
	5,000-10,000m	0.2067
	>10,000m	0.7352
Distance to conservation areas	<5,000m	0.0581
	5,000-10,000m	0.2067
	>10,000m	0.7352
Ecosystems (beaches, mangroves, corals and tidal wetlands)	<5,000m	0.0581
	5,000-10,000m	0.2067
	>10,000m	0.7352
Distribution of benthos	H' <1	0.7352
	1<H'<3	0.2067
	H>3	0.0581

3.3.2 Zoning Dredged Material Disposal

Zoning of suitable dumping area was performed through a weighted overlay of thematic layers of the criteria in Arc GIS 10.1.The GIS thematic layer of environmental criteria included four sub-layers of bottom depth, litho-hydrodynamics, ecosystems and benthic distribution. The GIS thematic layer of socio-economics was composed of four sub-layers of distance to residential areas, tourist sites, distance to shipping channels, distance to aquaculture area and distance to conservation areas. GIS thematic sub-layers of criteria with their weighted attributes were built in GIS database and then overlaid following multi-criteria GIS overlay analysis model (Figure 2). A new layer outcome showed one zone (green) at the range of above 0.5 to 0.65, being highly suitable for the dumping and the another zone (red and yellow) of under 0.5, being low suitable or not matching criteria for the dumping. Also, from the outcome of the MCOA (Figure 3), it shows that deep-sea areas (below 15m deep to the deeper), offshore to the South, Southwest have a higher suitability (values above 0.5) than other zones.

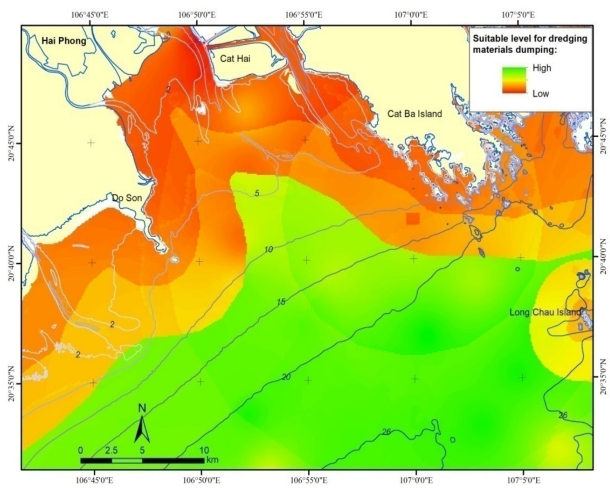

Figure 3. Zones of suitability for dredged material dumping

3.4 Discussions

Considering that being dredged from the shipping channels in Hai Phong, the environmental quality of dredged materials meeting the permissible limits issued by the Ministry of Natural Resources and Environment of Vietnam, the effects of turbidity and sedimentation by the dredged material dumping in coastal waters of Hai Phong ports are accepted when the dumping takes place in the highly suitable zone. The dispersion and sedimentation

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of dredged materials dumped into coastal waters can generally degrade marine and coastal ecosystems, pollute the waters used for economic activities such as tourism, aquaculture and fishing ... Therefore, the environmental impacts from disposal sites in the zone, when put into operation, will be focused on turbidity. Some recent studies in the study area found the existence of the maximum turbidity zone of the Cam River - Bach Dang estuary (EMT) with the maximum turbidity concentrated in the area of the saline intrusion and decreasing when salinity increases (1-15‰) [18], and could be spatially distributed up to 15km seaward from the coast during the low tide in the rainy season [18]. Thus, the area suitable for dumping is outside of the maximum turbidity zone and in the area with the sedimentation rate reaching about 10-20mm/ year [17]. It can be seen that the dredged material dumping at sites in this zone is quite suitable for the development trend of the bottom topography as well as ecological and environmental. The results of the 3-dimensional numerical model (3D) of the project DT.MT.2015.721 [3] also showed that, in the rainy and dry seasons, the turbid area from the depth below 15m to 25m for dumping would be expected to have a minor impact on the coastal area of Cat Ba islands in sea bad conditions that occur during the S, SW directional waves. The predicted cases with other wind and wave directions hardly affect the coastal areas of Cat Ba-Long Chau islands, Cat Hai coastal areas and Do Son beaches. Thus, the turbid waters caused by the dredged material disposals in the area are suitable because dredged material dispersion is only in a narrow range due to the diversion of the tidal currents. This turbid area in some cases has a minor impact on the coastal waters of Cat Ba with the concentration of suspended sediment increasing below 10mg/l in the bottom layer, not significantly in the upper layers.

The proposed appropriate zone for dredged material dumping will meet the increasingly urgent need of Hai Phong city. However, this area is located quite far from the dredging areas. This can increase the cost of transporting dredged materials from the dredging area to dumping sites. Transportation cost incurred for 1m^3 of dredged materials per 1km is estimated at VND 8,424 - this price applies to the transportation distance from km 6 onwards. Although this increases the cost of channel dredging, it may still be much lower than the environmental costs and losses incurring if dumping closer to shore. Therefore, it is not possible to place disposal sites closer as it may cause unpredictable impacts, especially impacts on the Cat Ba Biosphere Reserve and the coral areas surrounding Long Chau island.

4. Conclusions

Eight sub-criteria of sustainable development criteria of socio-economics and the environment developed and weighted included bottom depth, litho-hydrodynamics, ecosystems, distribution of benthos, distance to residential areas and tourist sites, distance to aquaculture area, distance to ecosystems and distance to conservation areas. These sub-criteria were developed in GIS platform and then analyzed using multi-criteria GIS overlay model. The analysis results show that the zone below 15m deep, to the South and Southwest is highly suitable than others for dredged material disposing. In the zone, the factors of topographical depth, low biodiversity, medium to relatively high sedimentation rate, minor negative impacts on important ecosystems meet criteria for sustainable management of coastal area of Hai Phong. The dumping of the dredged materials offshore in this zone may incur costs for the maintenance and dredging of shipping channels in Hai Phong. This issue requires further research in costs - benefits with the integration of environmental - ecological factors to ensure rational use of resources and environmental protection in coastal areas.

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