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Measurements of Wind-Stress Induced Positive and Negative Storm Surges During Hurricane Isaac

By S. A. Hsu

Louisiana State University

Abstract- When Hurricane Isaac in 2012 was over the coastal regions of Louisiana, USA, simultaneous measurements of both positive and negative storm surges were made by the U. S. National Ocean Service. Analysis of these datasets including wind speed and direction indicates that 93% of the positive surge and 74% of the negative surge can be explained by the wind-stress forcing, respectively. It is also found that the ratio of wind stress to either positive or negative surge is approximately 1:1.5, meaning that one pascal (1 N m^{-2}) wind stress can generate 1.5 meters of water-level increase or decrease. This ratio may be used for forecasting or hind-casting purpose.

Keywords: *hurricane Isaac · storm surge · wind stress · friction velocity.*

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Keywords: hurricane Isaac · storm surge · wind stress · friction velocity.

I. INTRODUCTION

Along the coast, storm surge is often the greatest threat to life and property from a tropical cyclone (TC) (see, e.g., <http://www.nhc.noaa.gov/surge/>,

and Rappaport, 2014). In general, positive surges are measured when the wind pushes the water from sea to land (see, e.g., Hsu, 2013, Lillibridge et al., 2013, Mas et al., 2015, Mehra et al., 2015) and negative surges occurred when the wind forces the water from land to the sea (e.g., Houston and Powell, 1994). During Hurricane Isaac in 2012 (see Figs. 1 and 2), simultaneous measurements of both positive and negative surges are available from the National Ocean Service (NOS) stations (see www.ndbc.noaa.gov) at SHBL1 and FRWL1, respectively (see Fig. 3). The purpose of this research note is to analyze these measurements and present formulas for practical applications.

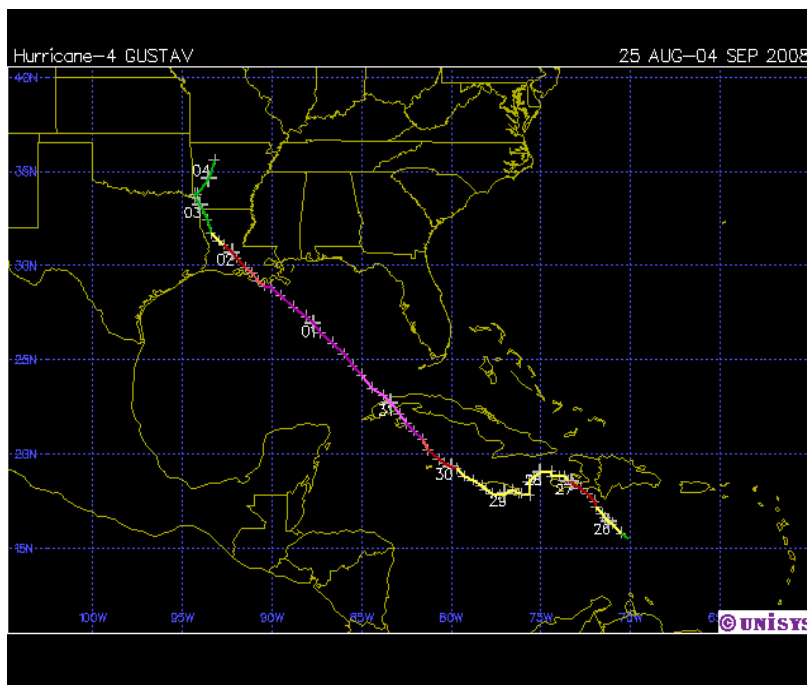


Figure 1: Track of Hurricane Isaac from 26 Aug. to 04 Sep. 2012 (Courtesy of <http://weather.unisys.com/hurricane/atlantic/2012H/index.php>). Note that hurricane force winds (from 18 UTC on Aug. 28 thru 17 UTC on Aug. 29, 2012) occurred over the Louisiana coastal regions.

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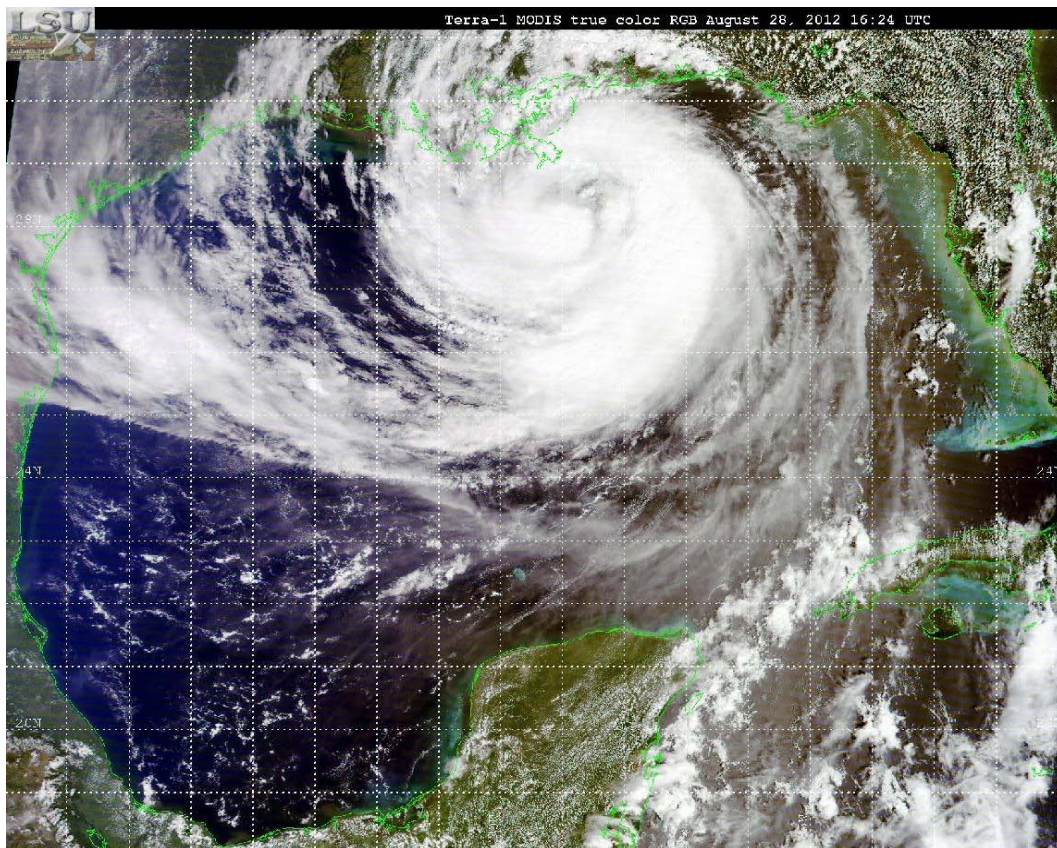


Figure 2: Satellite image of Isaac at 1624 UTC on Aug. 28, 2012 (Courtesy of the Earth Scan Lab, Louisiana State University, see www.esl.lsu.edu).

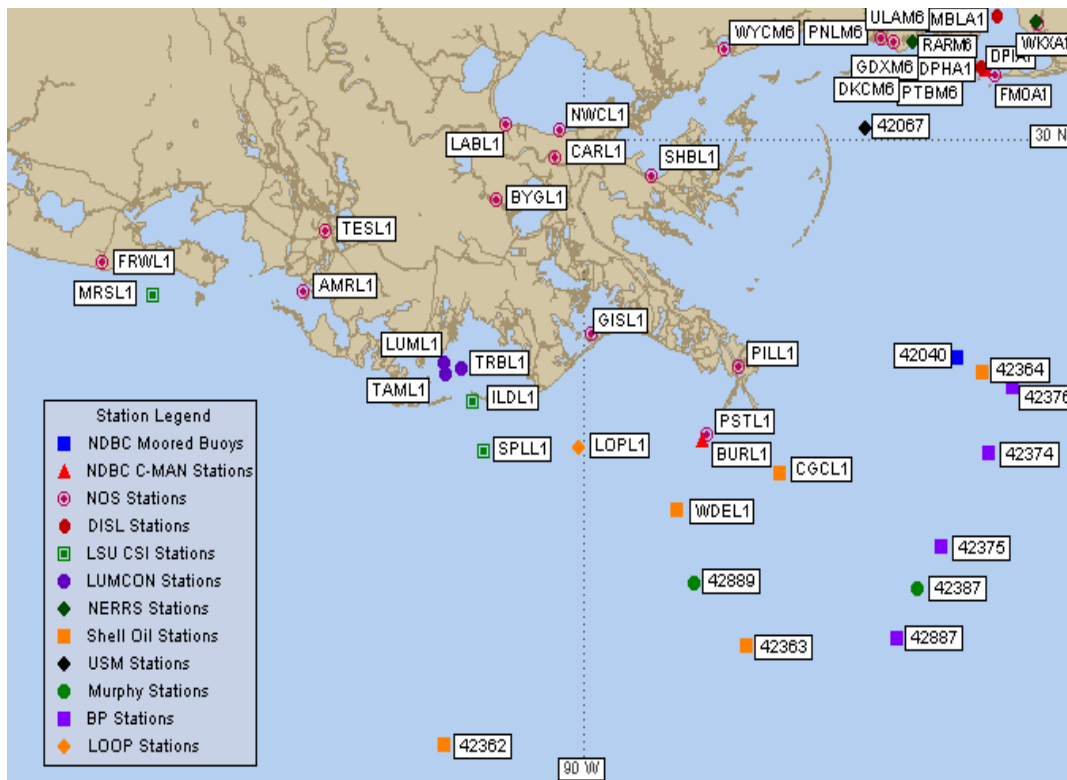


Figure 3: Locations of NOS stations at SHBL1 on the right hand side of the Isaac track east of New Orleans, Louisiana and FRWL1 on the left at the westernmost locale in the figure, see www.ndbc.noaa.gov).

II. METHODS

Before our methods are discussed, basic hydrodynamic equations related to the storm surge are

quoted from the Shore Protection Manual (1984, see pages 3-119 thru 3-121 for detailed explanation) as follows:

The differential equations appropriate for tropical or extratropical storm surge problems on the open coast and in enclosed and semienclosed basins are as follows:

$$\frac{\partial U}{\partial t} + \underbrace{\frac{\partial M}{\partial x} \frac{\partial M}{\partial x} + \frac{\partial M}{\partial y} \frac{\partial M}{\partial y}}_{\text{Advection of Momentum}} = \underbrace{fV}_{\text{Coriolis}} - \underbrace{gD \frac{\partial S}{\partial x}}_{\text{Surface Slope}} + \underbrace{gD \frac{\partial \xi}{\partial x}}_{\text{Inverse Barometer}} + \underbrace{gD \frac{\partial \zeta}{\partial x}}_{\text{Astro. Tide Potential}} + \underbrace{\frac{\tau_{sx}}{\rho}}_{\text{Wind Stress}} - \underbrace{\frac{\tau_{bx}}{\rho}}_{\text{Bottom Stress}} + \underbrace{W_x P}_{\text{Rainfall Rate}} \quad (3-77)$$

$$\frac{\partial V}{\partial t} + \underbrace{\frac{\partial M}{\partial y} \frac{\partial M}{\partial y} + \frac{\partial M}{\partial x} \frac{\partial M}{\partial x}}_{\text{Advection of Momentum}} = - \underbrace{fU}_{\text{Coriolis}} - \underbrace{gD \frac{\partial S}{\partial y}}_{\text{Surface Slope}} + \underbrace{gD \frac{\partial \xi}{\partial y}}_{\text{Inverse Barometer}} + \underbrace{gD \frac{\partial \zeta}{\partial y}}_{\text{Astro. Tide Potential}} + \underbrace{\frac{\tau_{sy}}{\rho}}_{\text{Wind Stress}} - \underbrace{\frac{\tau_{by}}{\rho}}_{\text{Bottom Stress}} + \underbrace{W_y P}_{\text{Rainfall Rate}} \quad (3-78)$$

An evaluation of the relative magnitude for the above terms is provided in USACE (1977) for Hurricane Camille, which also affected our study area. The most important finding of that evaluation is that approximately 80% of the total surge was caused by the wind stress in the x-component (used here for onshore component). Therefore, we postulate that, in order to investigate the contribution of wind stress to the total surge, the term of surface slope needs to be balanced by that of wind stress such that,

$$g D (dS/dX) = \tau_{sx} / \rho_{sea}, \quad (1)$$

$$dS = [dX/(gD\rho_{sea})] \tau_{sx} \quad (2)$$

$$S - S_0 = [X/(gD\rho_{sea})] \tau_{sx}, \quad (3)$$

$$S - S_0 = K\tau_{sx}, \quad (4)$$

$$\tau_{sx} = \rho_{air} U_*^2, \quad (5)$$

According to Andreas et al. (2012),

$$U_* = 0.0583 U_{10} - 0.243, \quad (6)$$

Following Carter (1982),

$$H_s = 0.0163 X^{0.5} U_{10}, \quad (7)$$

According to Hsu (2016), under hurricane conditions in the Gulf of Mexico,

$$H_s = 0.47 U_{10} - 3, \quad (8)$$

The symbols for above equations are: g = gravitational acceleration, D = water depth, S = total surge, S_0 = predicted astronomical tide, X = fetch, ρ_{air} and ρ_{sea} = air and sea-water densities, respectively, τ_{sx} = the wind stress, U_* = friction velocity, U_{10} = wind speed at 10m, and H_s = significant wave height. All units are in

SI except that the fetch is in km. Note that coefficient K in Eq. (4) can vary with X as shown in Eq. (3) (see, e.g., Irish et al., 2008). However, for a given wind speed, X may be considered as a constant based on Equations (7) and (8).

Using these aforementioned formulas or methods, we can now continue our analysis.

III. ANALYSIS AND RESULTS

a) Positive surges

Simultaneous measurements of wind speed and direction and water level were made by the NOS during Isaac. Pertinent datasets and analysis for the wind characteristics are presented in Figures 4 and 5, respectively. It can be seen that, from 0000UTC on 28 August to approximately 0400UTC on 29 August, onshore winds produced positive surge for more than 3 meters. Using the 6-minute datasets from NDBC (see www.ndbc.noaa.gov) for SHBL1 during this period, relation between the positive surge and wind stress is found and presented in Figure 6. Since the coefficient of determination, $R^2 = 0.93$, meaning that 93% of the variation between positive surge and wind stress can be explained by

$$S - S_0 = 1.5 \tau_{sx} + 0.13 \quad (9)$$

Since the correlation coefficient, $R = 0.96$, is very high, Eq. (9) may be useful operationally. Note that the wind stress can be estimated routinely from Equations (5) and (6) since $\rho_{air} = 1.22 \text{ kg m}^{-3}$ for the moist air (Zedler, 2009) and the wind speed is measured.

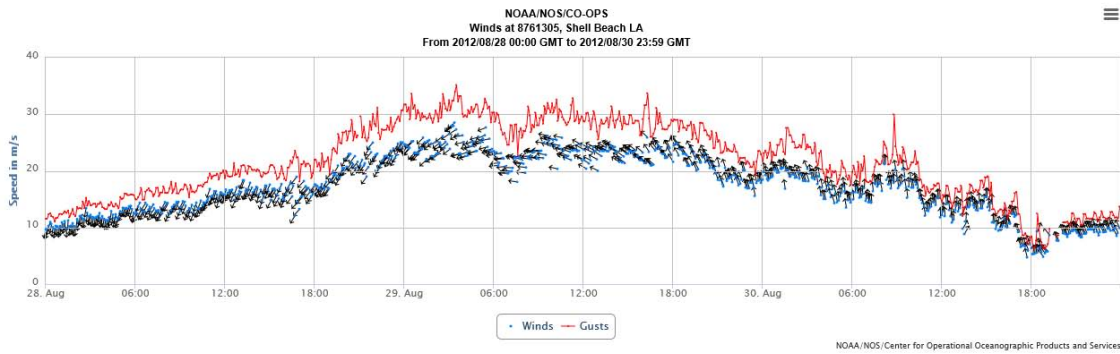


Figure 4: Measurements of wind speed, direction, and gust from 28 thru 30 August 2012 at NOS station SHBL1 during Hurricane Isaac (see www.ndbc.noaa.gov)

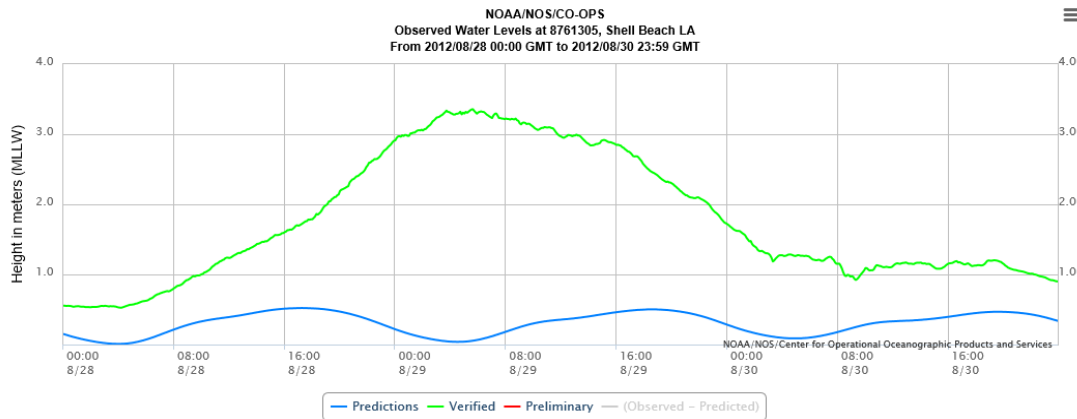


Figure 5: Measurements of total water level (in green) and predicted astronomical tide (in blue) during the period shown in Figure 4 (see www.ndbc.noaa.gov).

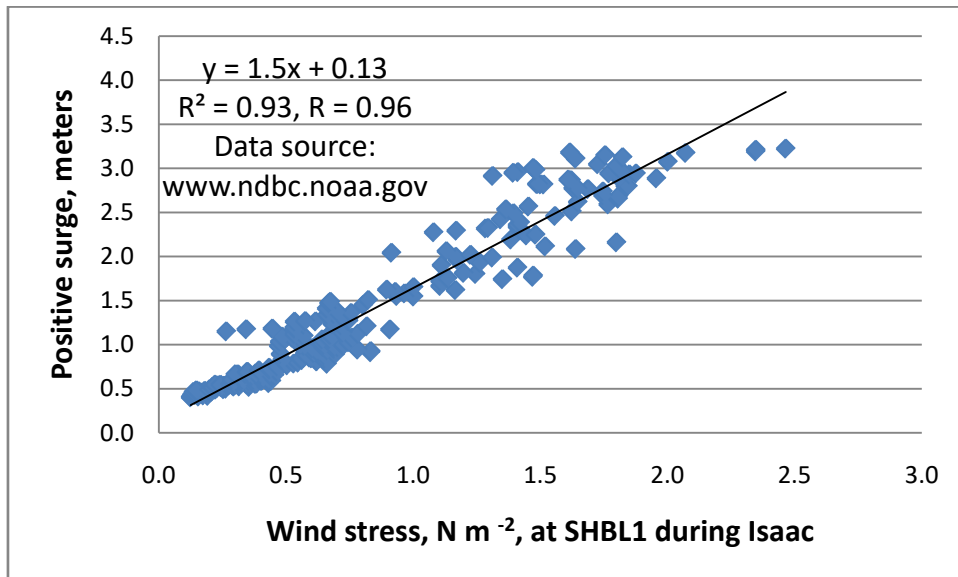


Figure 6: Relation between positive surge and the wind stress at SHBL1 during Isaac

b) Negative surges

Similar analysis for the negative surge is performed during the same period for FRWL1. Results are presented in Figures 7 thru 9. Therefore, for negative surge, we have

$$S - S_0 = - 1.4 \tau_{sx} - 0.19 \tag{10}$$

Note that, since $R = 0.86$, the wind stress also plays a dominant role in the boundary-layer physics of negative surge.

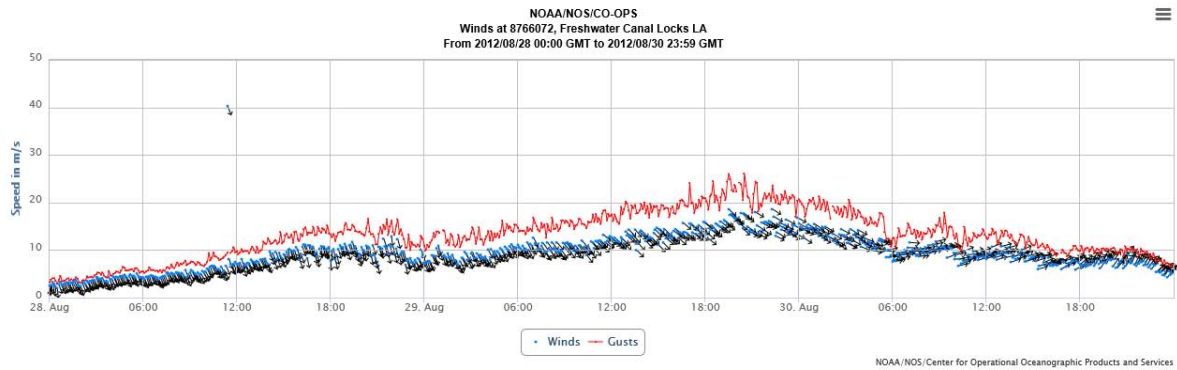


Figure 7: Measurements of wind speed, direction, and gust from 28 thru 30 August 2012 at NOS station FRWL1 during Hurricane Isaac (see www.ndbc.noaa.gov)

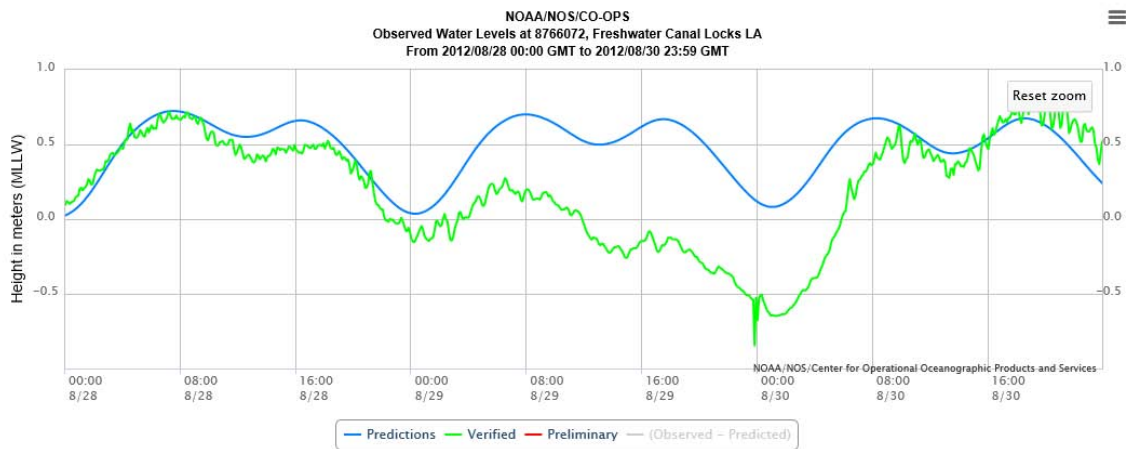


Figure 8: Measurements of total water level (in green) and predicted astronomical tide (in blue) during the period shown in Figure 7 see www.ndbc.noaa.gov).

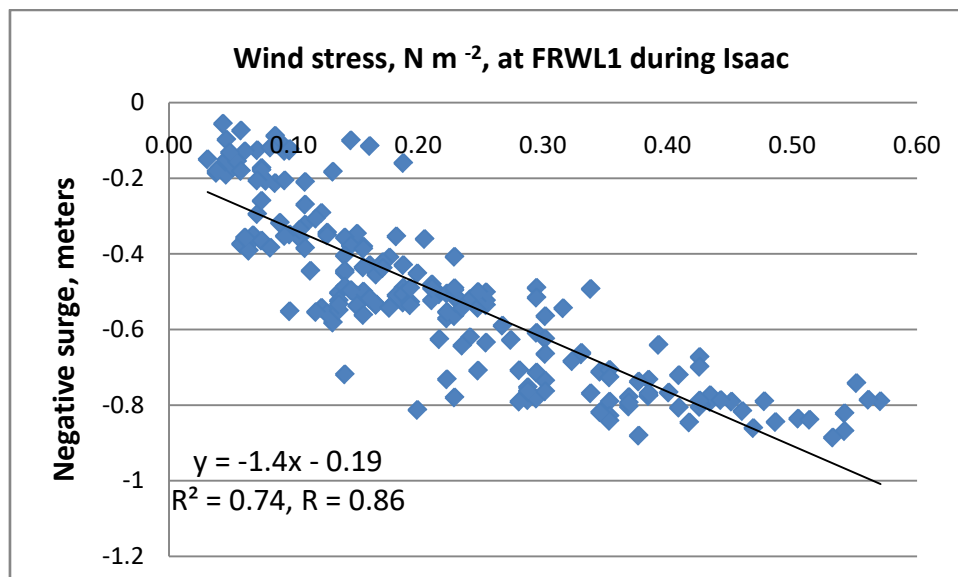


Figure 9: Relation between negative surge and the wind stress at FRWL1 during Isaac

IV CONCLUSIONS

On the basis of aforementioned analysis and discussion, it is concluded that

- (1) When the winds blow from sea to land during a TC, positive storm surges prevail. Its relation with the wind stress is presented in Eq. (9);
- (2) When the winds blow from land to the sea, negative surges occur. Its relation with the wind stress is shown in Eq. (10), and most importantly;
- (3) It is found that the ratio of wind stress to either positive or negative surge is approximately 1:1.5, meaning that one Pa (pascal = 1 N m^{-2}) wind stress can produce 1.5 meters of water-level increase or decrease. Using this ratio, it is possible to reconstruct or estimate the maximum wind stress or TC intensity from the maximum water level recorded in an area affected by a TC in the past, or to forecast future water level change caused by a TC.

V. ACKNOWLEDGEMENTS

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Preliminary Investigation of Some Biological Aspects of Length-Weight Relationship and Condition Factor of Periwinkle (*Tympanotonus fuscatus*, Linnaeus 1758) from Okrika Estuary

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University of Bremen

Abstract- Assessment of length-weight relationship and condition factor of a commercially important mollusc species, Periwinkle, *Tympanotonus fuscatus*, from Okrika estuary was conducted from October, 2015 to February, 2016. A total of 120 samples of the species were hand-picked from the mangrove ecosystem of Okrika. The results obtained showed that the gastropod species had negative allometric growth patterns with a growth exponent, b value of 2.18. This value was confirmed as negative allometric, because it was significantly different ($p < 0.05$) from 3 when a t-test was carried out. The mean condition factor, K of the species was 18.9, which indicated that they were in good condition during the sampling period.

Keywords: length-weight relationship; condition factor; periwinkles; okrika estuary.

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Preliminary Investigation of Some Biological Aspects of Length-Weight Relationship and Condition Factor of Periwinkle (*Tympanotonus fuscatus*, Linnaeus 1758) from Okrika Estuary

Running Title: Some aspects of ecology of Periwinkles

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Abstract- Assessment of length-weight relationship and condition factor of a commercially important mollusc species, Periwinkle, *Tympanotonus fuscatus*, from Okrika estuary was conducted from October, 2015 to February, 2016. A total of 120 samples of the species were hand-picked from the mangrove ecosystem of Okrika. The results obtained showed that the gastropod species had negative allometric growth patterns with a growth exponent, b value of 2.18. This value was confirmed as negative allometric, because it was significantly different ($p < 0.05$) from 3 when a t-test was carried out. The mean condition factor, K of the species was 18.9, which indicated that they were in good condition during the sampling period.

This study recommends that further research needs to be conducted because it is the first of its kind in this estuary and that the sampling duration was one-third of a year (4 months). Also efforts should be taken to reduce the pollution load in order to safe-guard this valuable resource for the local population.

Keywords: length-weight relationship; condition factor; periwinkles; okrika estuary.

I. INTRODUCTION

Periwinkle (*Tympanotonus fuscatus*, Linnaeus 1758) is a univalve, prosobranch gastropod (Mollusca) commonly found in the intertidal zone of brackish ecosystems in the Niger-Delta and other parts of West African coastal waters such as mangrove swamps, creeks, lagoons, estuaries (Nickles, 1950; Dambo, 1993; Jamabo *et al.*, 2009; Moruf and Lawal-Are, 2015). They usually inhabit soft substratum or mudflats rich in decaying organic matter and detritus (Jamabo and Chinda, 2010; Iboh *et al.*, 2015). Deekae (1987) reported that nature of bottom deposit, water depth and current are the major factors controlling the distribution of this

shellfish in the estuaries. When in their habitat, they migrate to the coastal edge and usually aggregate under the breathing roots of mangrove plant species such as *Avicennianitida*, *Rhizophora mangle* and *Nypa palm* for protection from the direct heat of sun (Cariton and Cohen, 2002). They have the ability to survive without water or wetting for a long period time especially during dry season but rely on their food reserve (Oyenekan, 1979). They provide a livelihood and nutrition for vast majority of people and have been important marine resources targeted worldwide. They constitute a major food item or delicacy of large number of people living in the Niger-Delta (Jamabo and Chinda, 2010). Millions of *T.fuscatus* are transported in jute bags on a daily basis to the markets for sale. It is a relatively cheap source of animal protein and its shell is commonly used as source of calcium and phosphate in livestock feed and as ornaments (Jamabo *et al.*, 2009; Akwari and Archibong, 2011; Bob-Manuel, 2012). This species also has some medicinal values. For instance, because of its high iodine content, it has been used for the treatment of endemic goitre (Bob-Manuel, 2012).

No effort has been made to culture this species in captivity, therefore harvest from the wild has mounted high pressure and impact on its abundance, large-size and community structure (Powell *et al.*, 1985; FAO/FIDI, 1994).

Length-Weight relationship (LWR) indicates the average weight of fish at a given length by making use of amathematical equation to show relationships between the two (Beyer, 1987). Fish can attain either isometric or allometric growth (Gayaniilo and Pauly, 1997; Sakar *et al.*, 2013). Isometric growth indicates that both length and weight of the shellfish are increasing at the same rate. Allometric growth can either be positive or negative. Positive allometric implies that the shellfish becomes stouter or deeper-bodied as its length increases. Negative allometric implies the shellfish becomes slender as its length increases.

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Condition Factor (CF) is an estimation of general well-being of fish (Oribhabor *et al.*, 2011) and is based on the hypothesis or assumption that heavier fish (at a given length) are in better condition than the lighter ones (Bagenal and Tesch, 1978; Ogamba *et al.*, 2014). The condition factor of 1.0 or greater indicates the good condition of fish while less than 1.0 shows bad condition (Abobi, 2015). The condition factor can be influenced by season, sex, type of food organism consumed by fish, age of fish, amount of fat reserved and environmental conditions (Bagenal and Tesch, 1978; Anene, 2005; Abowei, 2009).

Length-Weight relationship and Condition Factor are important tools in fisheries biology, management and stock assessment to support data about standing stock biomass, their well-being, compare ontogeny of fish population and growth pattern studies of fish from different regions, understand their life cycles and span, construct ecosystem modelling and can be used as index to assess the status of the aquatic environment where the fish live (Le Cren, 1951; Beyer, 1987; Bolger and Connoly, 1989; Patrakis and Stergiou, 1995; Montopoulos and Stergiou, 2002; Mendes *et al.*, 2004; Anene, 2005; Fafioye and Oluajo, 2005; Imam *et al.*, 2010; Lawson *et al.*, 2013; Ogamba *et al.*, 2014).

Few studies have been conducted on the length-weight relationship and condition factor of periwinkles in some parts of the Niger-delta (Jamabo, 2007; Jamabo and Chinda, 2010; Udoh, 2013; Iboh *et al.*, 2015). Niger-Delta is the crude-oil reservoir of Nigeria and all aspects of the industrial activities, from exploration, production to waste discharge, have adverse effects on the ecosystems (Uzoma and Mgbemena, 2015). The impact of environmental damage in the region cannot be quantified (Baghebo *et al.*, 2012).

There is no published research on some of the aspects of the biology of periwinkle (*T.fuscatus*) in the highly polluted, environmental-unfriendly Okrika estuary. This study is therefore aimed at providing first hand and baseline information on the aspects of the ecology (length-weight relationship and condition factor) of this species in the Okrika estuary.

II. MATERIALS AND METHODS

a) Description of the Study Area

The study area (Figure 1) lies between latitudes 4° 44' 00" to 4° 46' 10" N and longitudes 7° 5' 15" to 7° 6' 15" with an area of 905.2sq.km. It is located in Okrika Local Government Area of Rivers State with a population of over 150,000 (NPC, 2006). *Okrika estuary* has an average length of 21km and lies in the north bank of the Bonny River with a distance of about 56km from the Bight of Benin in Eastern part of the Niger-Delta. It is a mangrove environment characterised by regular salt water inundation as a result of tidal action and flooding

and extensive sandy bottom and mud-flat. The tidal amplitude ranges between 1.5-2m in normal tide. It originates from Marine Base and runs through *Okari* and crosses the Mainland to *Ekerekana Ama* and other creeks such as *Sandfilled/Mainland Bridge (Ogoloma)*. It is characterized by tropical climate with alternating wet (March to October) and dry (November to February) seasons. Based on the Nigerian Meteorological (NIMET) data, the area is associated with warm temperature ranging from 26° to 34°C, annual bimodal rainfall of 2300-4000 cubic metres and distinct relative humidity and evaporation. It is ecologically endowed with vast biodiversity; fish, mollusc, crustaceans, crabs, *Rhizophora mangle*, *Laguncularia racemosa*, *Avicennia africana*.

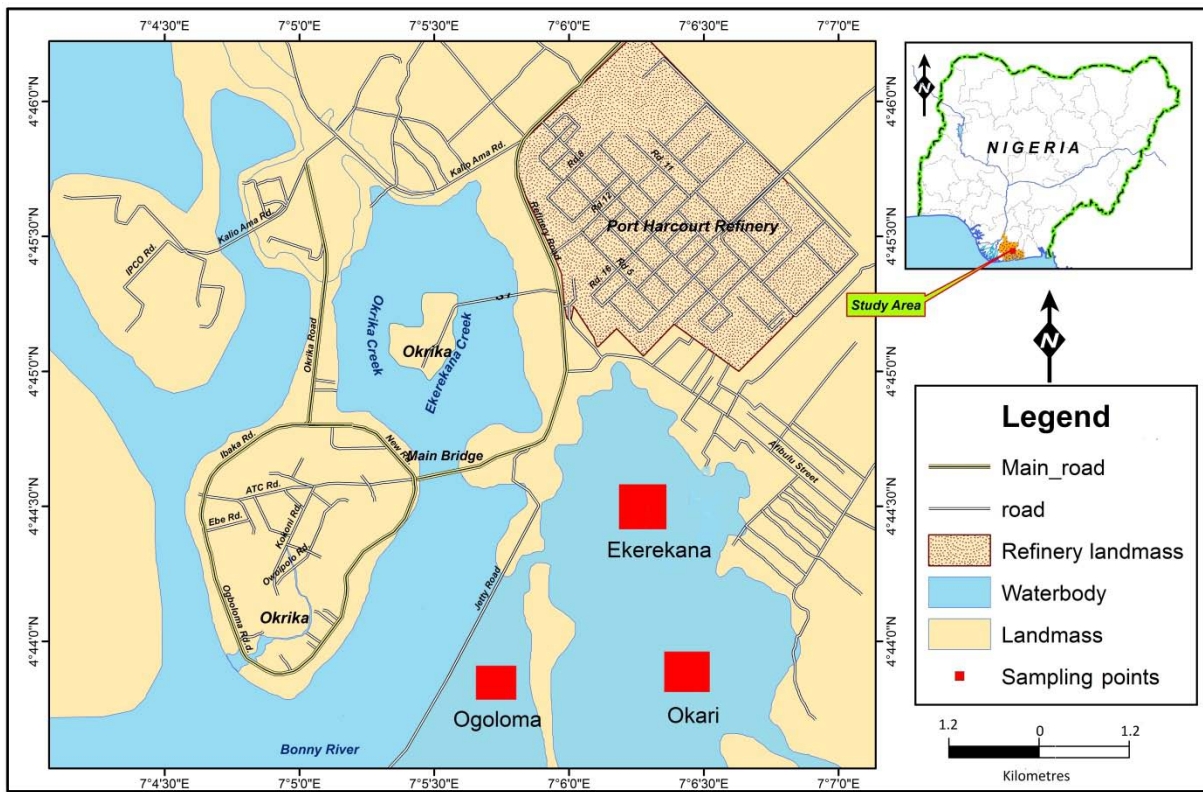


Figure 1: Map of Okrika estuary showing the sampling stations

b) *Experimental Design*

Three experimental sampling sites along the estuary course were utilized for data collection. Each site is about 1 - 2km from the other. The respective sampling sites were represented as *Ekerekana (EKR)*, *Okari (OKR)* and *Ogoloma (OGL)*. These sites were chosen because *T.fuscatus* are mostly found and aggregated in these sections of the mangrove ecosystem and also their proximity to the refinery discharge point and in addition to other activities such as domestic waste and sewage disposal, oil-bunkering and transportation carried out along its course and also due to their abundance, availability, economic importance, mostly eaten by the populace (market survey), feeding habits and prevailing environmental conditions. Sampling was done in October/November, 2015 and January/February, 2016 which represent the peak of both the wet and dry seasons respectively.

$$\text{Shell-fish} = 3 \text{ Sites} * 20 \text{ Replicates} * 2 \text{ Seasons} = 120 \text{ Samples}$$

c) *Periwinkle collection, Preservation and Identification*

The periwinkle samples were hand-picked randomly from each sampling site at low or ebb tide. Sampling was done in accordance with the techniques used by other published literatures (Jamabo *et al.*, 2009; Moruf and Lawal-Are, 2015). All samples collected were placed in polythene bags. They were transported to the laboratory on ice in a cold chest and washed off mud on getting there. In the laboratory, they were identified to

the species level using the fish catalogue of FAO (Fischer *et al.*, 1981; FAO, 1990; Schneider, 1990). Their morphometrics of shell total length (STL) and weight (BWt) were measured using a graduated plastic measuring board and a sensitive scale balance (Kern 440-35A model) (Moruf and Lawal-Are, 2015). All lengths and weights were measured in centimetres and grams respectively. The data gathered were used to evaluate the relationship between the shell total length (STL) and weight (BWt) of *T.fuscatus*.

III. DATA ANALYSIS

a) *Length-Weight Relationship (LWR)*

The raw data of shell total lengths (STL) and weights (BWt) of the periwinkles collected were used to compute the length-weight relationship with the formula;

$$W = aL^b \dots\dots\dots (1)$$

(Le Cren, 1951; Ricker, 1973)

where W = body weight, L = total length, a = intercept on the length axis, b = slope or regression coefficient which usually ranges from 2 to 4.

Equation (1) is log transformed to give a linear relationship;

$$\text{Log } W = \text{Log } a + b \text{ Log } L \dots\dots\dots (2)$$

(Le Cren, 1951; Parson, 1988)

When Log W is plotted against Log L, the regression coefficient or growth exponent, b, and intercept, a are obtained.

For each species, the growth exponent (b) was compared to 3 using student's t-test to ascertain whether species grow isometrically or not (Sokal and Rohlf, 1987). This was achieved by using the formula;

$$t_s = b - 3 / s_b \dots\dots\dots$$

(Zar, 1984; Morey *et al.*, 2003)

t_s = student's t-test, b = slope, s_b = standard error of the slope.

IV. CONDITION FACTOR

This was computed for each species with Fulton's equation;

$$K = 100 \times W/L^b \dots\dots\dots$$

(Ricker, 1971; Pauly, 1983)

where K = condition factor, W = body weight, L = total length

V. STATISTICAL ANALYSIS

The data obtained from the morphometric analysis were subjected to statistical analysis using R-Studio Version 0.98.1083 (2009-2014) and Excel version. Analysis of variance (ANOVA) was used to test whether the calculated regression line was significant (Ogbeibu *et al.*, 2005). All statistical analyses were considered at significant level of 5% ($p < 0.05$).

VI. RESULTS

a) Length-weight relationship

A total of 120 samples of *T.fuscatus* were measured for their morpho-metrics from October 2015 to February 2016. The shell total lengths (STL) and weights (Bwt) ranged from 2.5 – 4.8cm (mean of 3.27 ± 0.29) and 1.16 – 5.87g (mean of 2.54 ± 0.57), respectively.

The length-weight relationship was determined using logarithmic transformation. The linear relationship of the log-weight and log-length is shown as;

$$\text{Log Bwt} = -1.67 + 2.18 \text{ Log STL} \dots\dots$$

(Table 1)

The intercept, a, was negative and the growth exponent, b (2.18), when compared with 3 using t-test showed that there was a significant difference (p -value < 0.00001) confirming the growth pattern of *T.fuscatus* to be negative allometric.

The relationship between shell total length and weight showed a highly significant positive correlation, $r = 0.81$, $p < 0.001$. The scatter plot or regression graph of the shell total length and weight relationship of the species is shown in Figure 2. This reflects the exponential growth in weight with increasing length. The statistics of the regression is shown in Table 1.

b) Condition Factor (K)

The mean K value of *T.fuscatus* for the sampling period in the study area was found to be 18.9 (Table 1).

Table 1: Morphometrics, Length-weight relationship and Condition Factor of *Tympanotonus fuscatus* from the study area

Species	Mean STL (cm)	Mean Bwt (g)	a	b	Type of growth	r	p-value of r	Mean K	t-value
<i>Tympanotonus fuscatus</i>	3.27 ± 0.29	2.54 ± 0.57	-1.67	2.18	-A	0.81	$2.2 \times 10^{-16} \dots$	18.9	8.542

Bwt = shell or body weight, STL = shell total length, a = intercept of the regression, b = slope of the regression (growth exponent), -A = negative allometric growth, r = correlation coefficient of length weight relationship, p-value of r = significance of correlation, K= Condition Factor, t-value = absolute value of t-test parameter to compare calculated slope to 3. *** $p < 0.001$

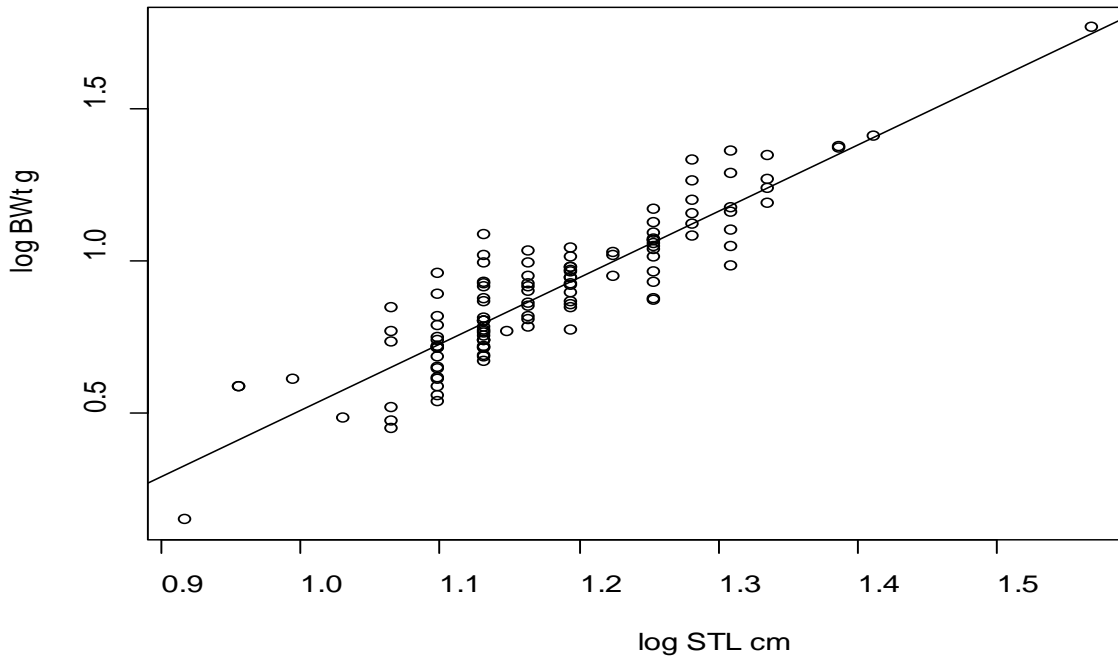


Figure 2: Length-weight relationship of *T. fuscatus*

VII. DISCUSSION

The correlation coefficient ($r = 0.81$) for length-weight relationship (LWR) was high for *T.fuscatus* which indicates a strong correlation and allows a fair prediction of weight for a given length. This agrees with earlier studies involving the same species from different parts of Niger-Delta (Jamabo *et al.*, 2009; Udoh, 2013). The value for growth exponent, b , obtained for the species is within the limit or range of 2 and 4 reported for most shell-fish (Tesch, 1971). The growth pattern of *T.fuscatus* was found to be negative allometric ($b = 2.18$), which indicates that the mollusc increases in weight faster than the length (Jamabo *et al.*, 2009). This finding agrees with Gabriel (1981), Jamabo *et al* (2009), Udoh (2013) and Moruf and Lawal-Are (2015), who reported the same growth pattern for this species in the Port-Harcourt area, Bonny and Cross River Estuaries (Niger-Delta) and Lagos Lagoon.

The high mean K value of 18.9 shows that the species samples were in favourable conditions although the creek receives refinery effluents in large amounts on a daily basis, but this could have been flushed out from the basin during high tide (Gunster *et al.*, 1993). Essienet *al* (2013) also reported a better healthy status (K) of range, 24.7-54.7, for this species investigated in oil polluted Qua-Iboe Estuary, Niger-Delta. High mean K values of 8.0 and 16.1 were also obtained for this species in Lagos Lagoon, but contradict the low K value < 1 reported by Udoh (2013) in the Cross River estuary. This mean K value could have been influenced by food

abundance and availability, foraging behaviour of this species, dependence on reserved or stored food energy and favourable environmental conditions such as salinity, temperature (Incze *et al.*, 1980; Brown and Hartwick, 1988; Moruf and Lawal-Are, 2015). As they are filter feeders, high phytoplankton levels could strongly influence their growth rates and final sizes. The high K value could also be explained probably because they were sampled when they were not breeding. This statement contradicts Egonmwan and Odiete(1983) and Ajao and Fagade(1990), who reported that their spawning, oviposition and early embryonic development are restricted to the beginning of the dry season months from November to January. During this period, their condition factor is expected to drop as they are spawning or breeding. This good healthy condition could also be attributed to their ability to tolerate and adapt to highly variable contaminated, environmental vagaries due to their genetic make-up as a molluscan (Mallet and Haley, 1983) and developing a regulatory mechanism for the toxicants by binding them to metallothioneins, converting it to non-toxic, soluble and excretory form (Viarengo and Nott, 1993; Viarengo *et al.*, 1999; Rainbow, 2002; Choi *et al.*, 2008). Banci *et al* (2017) explained that increased mutation rate of aquatic biota by toxic compounds like heavy metals can lead to high genetic variation and adaptability of fauna in locations with high quantities of such pollutants. In addition, the mollusc could also retract into shell which provides valuable protection for the tissues from environmental stress of pollution.

VIII. CONCLUSIONS AND RECOMMENDATION

This study provided information on the biology (LWR and condition factor) of a commercially important mollusc, *Tympanotonus fuscatus*, in Okrika creeks which is the first documented report of its kind and would serve as a reference point for future research.

The findings of this study suggest that the condition of the estuary is favourable to the mollusc in terms of availability and abundance of food resources. In addition, they might have developed a strategy to cope and adapt to an environment that receives effluents from a nearby crude oil refining company. Waste effluents disposed into these creeks are flushed out during high tides creating a favourable environment for the species investigated at least during part time. Further studies need to be carried out because sampling duration (4 months) might be too small to justify and make concrete conclusions.

The brackish ecosystem of Okrika creeks produces a valuable shellfish species for the local population. Therefore, measures must be taken to reduce the pollution impact on the aquatic ecosystem.

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Conflict of Interest

The authors declare that they have no competing interests among themselves.

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Reducing Greenhouse Gas Emissions from Ships through Analyzing of Marginal Abatement Cost (MAC) Curves

By Tien Anh Tran

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Abstract- The human is facing two big problems: The weather climate changes and energy crisis. There are a lot of causes to make above issues. One of them is a phenomenon of Greenhouse Gas emissions from industrial activities and humans. In my researching field, the author concentrates on studying how to reduce the Greenhouse Gas emissions from transportation ships using studying the Marginal Abatement Cost (MAC) curves applying to all ships. In purpose of researching that creates green shipping in the changeable climate condition nowadays.

Keywords: *greenhouse gas emission, marginal abatement cost, climate changes.*

GJSFR-E Classification : *FOR Code: 829802*



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1. INTRODUCTION

International shipping contributes with approximately 2.4% of global anthropogenic greenhouse gas (GHG) emissions, and its share is expected to increase in the future (International Maritime Organization, 2014), GHGs from shipping include mainly carbon dioxide (CO₂), methane (CH₄) and dinitrogen oxide (N₂O), of which CO₂ dominates the global warming potential. In addition, ships also emit other gasses with climate impact such as black carbon which has a warming potential and sulphate particles which have a cooling effect.

Energy efficiency measures are important to implement in order to decrease fuel use, but significant reduction in GHG emissions can be achieved only by the replacement of fossil fuels with renewable fuels. Energy efficiency can be defined by the relationship between the benefit or performance of a service and the energy input.

In fact, CO₂ emissions from the shipping sector rose substantially in recent decades as global trade and production continued to expand. Because ships are by far the most energy-efficient means of moving goods, shipping-sector emissions are expected to continue to grow even as rising oil prices encumber growth in other transportation modes.

In recent years, social interest on global warming issues has grown increasingly in recent years and topics related to energy conservation and reduction

in CO₂ emissions is omnipresent. International efforts to reduce the impact of climate change started primarily in Rio in 1992 where the framework for sustainable development was agreed by more than 150 governments. This was followed by adoption of the Kyoto Protocol in 1997 which bound the Annex I nations to reduce GHG emissions to an average of 5.2% below 1990 levels, by 2012. Although ships are the most fuel efficient mode of mass transport, the Second International Maritime Organization (IMO) GHG Study 2009 identified a significant potential for further improvements in energy efficiency mainly by the use of already existing technologies. Due to its international nature, marine transportation could not be directly handled through the Kyoto Protocol by Annex I countries. Instead, they are tasked to work through IMO. Political and public pressures have therefore been mounting on IMO, being a reasonable organisation for international shipping under climate change conventions, to act, see IMO publications in the references.

Marginal abatement cost (MAC) curves are a staple of policy discussions where there is a need to illustrate the incremental contributions of parts to a whole. In the instance, they provide a simple and elegant way to illustrate greenhouse gas emission (GHG) reductions from design standards, retrofit technologies, and operational measures that improve ship energy efficiency relative to their costs.

The first generation of MAC curves for marine GHG reductions effectively stimulated discussion about measures and standards but lacked detail. Development of more tailored policies for the industry requires MAC values with greater resolution, so that they are more applicable to specific ship types in the context of future trends. Such policies are critical to creating appropriate incentives and market signals in a diverse and competitive industry. Policies based on more general, low-resolution data are more likely to lead to unintended inequities and poorly matched incentives.

This article is divided into these sections: Section 1, Introduction; Section 2, Greenhouse gas emission from ships; Section 3, Applying the MAC curves for ship types and technical measures; Section 4, Results and Section 5, Conclusion.

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II. GREENHOUSE GAS EMISSION FROM SHIPS

MEPC 67 (Marine Environment Protection Committee) approved the Third IMO GHG Study 2014, providing updated emission estimates for greenhouse gasses from ships. According to estimates presented in this study, international shipping emitted 796 million tonnes of CO₂ in 2012, that is, about 2.2% of the total global CO₂ emissions for that year. By contrast, in 2007, before the global economic downturn, international shipping is estimated to have emitted 885 million tonnes of CO₂, that is, 2.8% of the total global CO₂ emissions for that year.

IMO's Marine Environment Protection Committee (MEPC) has given extensive consideration to control of GHG emissions from ships and finalized in July 2009 a package of specific technical and operational reduction measures. In March 2010 MEPC started the consideration of making the technical and operational measures mandatory for all ships irrespective of flag and ownership. This work was completed in July 2011 with the breakthrough adoption of technical measures for new ships and operational reduction measures for all ships, which are consequent, the first ever mandatory global GHG reduction regime

for an entire industry sector. The adopted measures add to MARPOL Annex VI a new Chapter 4 entitled "Regulations on energy efficiency for ships" making mandatory the Energy Efficiency Design Index (EEDI) for new ships and the Ship Energy Efficiency Plan (SEEMP) for all ships. The regulations entered into force through the tacit acceptance procedure on 1 January 2013 and apply to all ships over 400 gross tonnages and above.

The IMO predicts that tonne-miles of goods moved globally will increase 2% to 4% annually between now and 2050. This substantial industry growth translates to a near tripling of GHG emissions by 2050. It is estimated that GHG emissions from international shipping contribute to domestic and inland ships in 2007, for a total of 1050 mmt. At current rates of increase, shipping –sector CO₂ is expected to climb to between 2,500 mmt and 3,650 mmt by 2050. As of 2007, domestic and international shipping CO₂ emissions accounted for 3.3 percent of the global total. As the world economy's reliance on the global trade of goods, materials, and petroleum continues to rise, this figure is estimated to climb to between 2,500 mmt and 3,650 mmt by 2050.

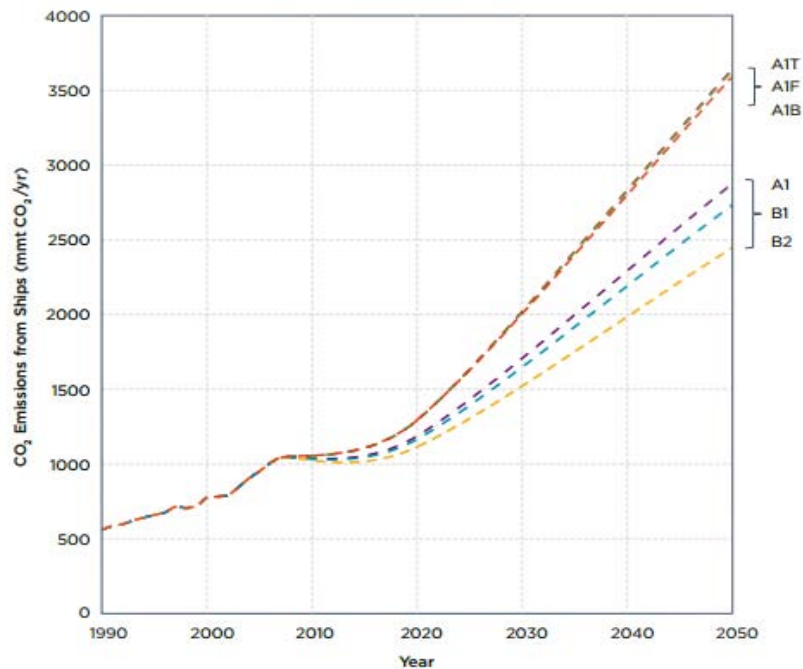


Figure 1: Projected growth of CO₂ emissions from shipping

A1F, A1B, A1T, A2, B1, and B2 are emission growth scenarios based on global differences in population, economy, land-use and agriculture. The six scenarios were used by the IMO Expert Group to form six growth scenarios for the shipping industry.

Figure 1 shows IMO projections of GHG growth based on six scenarios with varying assumptions for efficiency improvements, international trade growth, and GDP growth [5]. These estimates assume business as usual with little change to either economic growth rates

or the composition and activity of the world's shipping fleet. Regulatory proposals before the IMO in 2011 could have significant impact on these projections, either by gradually increasing the overall efficiency of the shipping fleet or by increasing the tonne-mile cost of goods. But

to meet ambitious CO₂ reduction goals, even more profound changes will be needed.

III. APPLYING THE MARGINAL ABATEMENT COSTS (MAC) CURVES FOR SHIP TYPES AND TECHNICAL MEASURES

The Marine Environment Protection Committee (MEPC) has been referred to a study of the greenhouse gas emissions from ships, first published in 2000 and updated in 2009 as the Second IMO GHG Study 2009, and presented at MEPC 59. The Second IMO GHG Study shows the social cost of some existing technical and operational measures. Policy makers and stakeholder have identified a range of abatement measures that are available or under development to slow the growth of energy consumption and CO₂ emissions from marine shipping. However the full cost accounting and assessment of effectiveness has been sparse. The cost-effectiveness of individual measures and of sets of measures is of increasing interest to policy makers, ship designers and builders, and existing ship owners.[6] Furthermore, some researches also indicated that estimate of CO₂ emissions reduction potential and associated marginal abatement costs for 14 types of new and existing ships as defined by the International Maritime Organization's (IMO) Greenhouse Gas (GHG) Experts Group. [7] Abatement cost is the cost of reducing environmental negatives such as pollution. Marginal cost is an economic concept that measures the cost of an additional unit. The Marginal Abatement Cost (MAC) measures the cost of reducing one more unit of pollution. [11] Marginal Abatement Cost method includes six steps like as:

- Identification of CO₂ abatement technology;
- Calculation of the cost-effectiveness of individual measures;
- Evaluation of the sensitivity to input parameters;
- Identification of constraints and barriers to implementation;
- Rank ordering technologies;
- Calculation of Marginal Abatement Cost Curve (MACC) as a function of ship type.

The first step identified CO₂ abatement technologies and operational measures. This was done through a comprehensive literature survey, a web-based survey and contacts with experts and technology users. The identification included collecting data on costs and abatement potential. [8]

The second step was the calculation of the cost-effectiveness of individual measures. Cost-effectiveness is by definition the quotient of costs and effect. This is also referred to as marginal abatement cost (MAC). CO₂ abatement technology often requires an investment in new technology. Generally, the technology requires maintenance and other operational

costs. Since installing the technology may take time and cargo space, there may be opportunity costs involved (the time and space could have been used to generate revenue) due to loss of service. In addition, there are fuel savings which are a negative cost or a benefit. The cost-effectiveness is the total annual costs divided by the CO₂ abated per year. The discount rate used to annuitize capital costs reflects the cost of capital of the maritime industry. (8)

On the other hand, based on the description above, the model of the cost function is installed with new technology and indicated in Equation 1 below.

$$\Delta C_j = K_j + S_j - E_j + \sum O_j \quad (1)$$

In where:

ΔC_j is the change of annual cost of the technology j;
 K_j is the capital cost of the technology j, discounted by the interest rate and written down over the service years of the technology or the remaining life time of the ship, which ever is shortest;
 S_j is the service or operating costs related to use the technology;
 $\sum O_j$ is the opportunity cost related to lost service time and space due to the installation of the technology;
 E_j is the fuel expenditure savings from that technology, which is a product of the price of fuel and the saving of fuel as described in Equation 2.

$$E_j = \alpha_j.F.P \quad (2)$$

Where

α_j is the fuel reduction rate of technology j;
 F is the pre-installation or original fuel consumption for a ship;
 P is the fuel price.

The original fuel consumption of a ship of a certain type, size and age is taken from the IMO 2009 GHG study. It is assumed to be constant over time so therefore the baseline does not need to make assumptions about which technologies would be used to achieve business-as-usual (BAU) energy –efficiency improvements.[8]

For each measure, costs associated with use of each identified ship type were determined. These included the cost of purchasing, installing, and operating, as well as any lots profits due to opportunity costs. Because these cost may vary significantly for ships of different types, sizes, and ages, a total of 53 ship type and size combinations were considered. These combinations were further applied to 6 different age bins spanning an assumed 30 year life. Altogether, we analyzed the marginal abatement costs associated with each measure for 318 ships types, sizes, and age combinations. The costs of each combination were then sorted and ranked. A simplified version of the calculation appears in equation (3):

$$MAC = \frac{\Delta C_j}{\infty_j \cdot CO_2} = \frac{K_j + S_j - E_j + \sum O_j}{\infty \cdot CO_2} \quad (3)$$

In where: ΔC_j : Capital cost;

$K_j = \Delta C_j$ discounted by the interest rate and service years;

S_j : Service cost of the measure;

$\sum O_j$: Opportunity cost related to lost service time due to the installation of the energy-saving measure and the discounted costs related to alternative uses of capital;

E_j : Energy savings from that energy-saving measure, which is a product of the price of energy and the saving of energy;

∞_j : Energy reduction rate of energy-saving measure j ;

CO_2 : Original CO_2 emissions from a ship.

The third step was the evaluation of the sensitivity to input parameters. It is performed a sensitivity analysis for fuel prices and discount rates.

The fourth step was the identification of constraints and barriers to implementation. The technical barriers for each individual measures that based on information from manufacturers, users of the technology, and other experts. In addition to that several general barriers and constraints were identified.

The fifth step was to rank order technologies based on their cost-effectiveness. The rank-ordering was done separately for each of the 318 different combinations of ship type, size, and age that were considered in our model. Of course, for each combination of ship type, size and age only those technologies were rank ordered that can be implemented on those ships. [8]

The sixth step was to develop Marginal Abatement Cost Curves (MACC). MACC are plots of the cost effectiveness of additional measures against the resulting cumulative reduction in CO_2 emissions. For each combination of ship type, size and age, there are a

suite of technical and operational measures that can be applied together. In other words, the cost and effectiveness are not a simple summation. Moreover, if different measures are implemented on the same ship, the cost-effectiveness of the measures changes because the effect of each additional measure is reduced by the fuel savings realised by previous measures. The construction of a MACC assumed that the most cost effective option (which is the option with the highest net present value) would be implemented first, the next most cost effective option second, and so on. [8]

Once calculated, mutually exclusive measures were compared based on cost effectiveness for each ship category. To develop the MAC curve, the 15 categories are ranked based on their marginal abatement cost, with the least expensive option assumed to be implemented first, followed by the second-least expensive, and so on for all measures. Because some measures will have lower CO_2 abatement potential as they are applied after other measures, marginal costs of subsequent measures were adjusted where previous measures would dilute their effectiveness.

Charting the 15 categories of efficiency measures beginning with the least expensive yields the marginal abatement cost curve. Figure 2 and Figure 3 show the aggregate curve and the contributing curves for each ship type. Comparing the marginal abatement costs in this manner shows that the majority of potential emission reductions, 340 mmt out of a total 436 mmt, could be reduced at negative marginal cost. This is equivalent to a central bound value of 33% potential reductions from projected improvements versus business as usual by 2020. 26% of these improvements can be had with negative cost. The lower and higher bounds for total potential emission reductions are 20% and 46%.

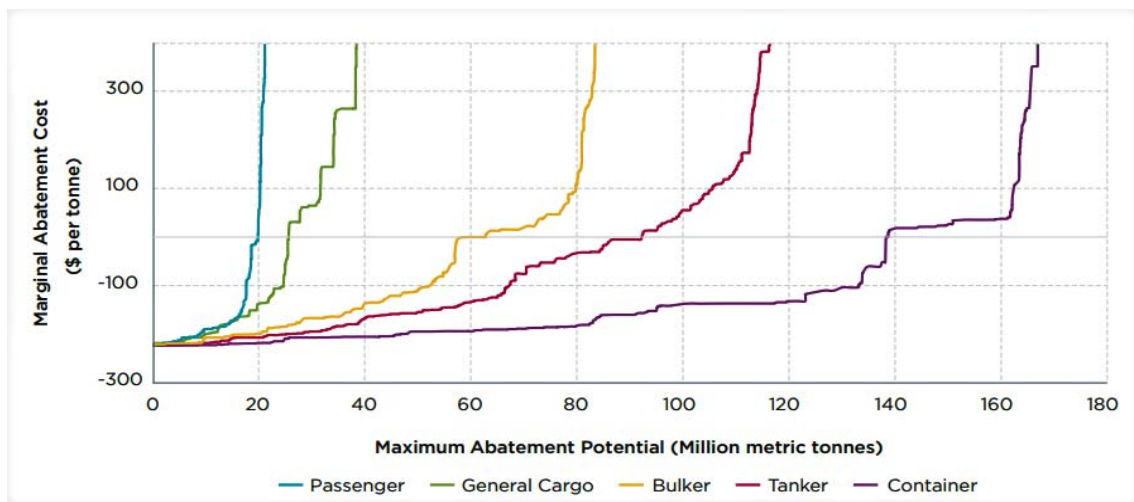


Figure 2: Central estimate of abatement potential by ship type

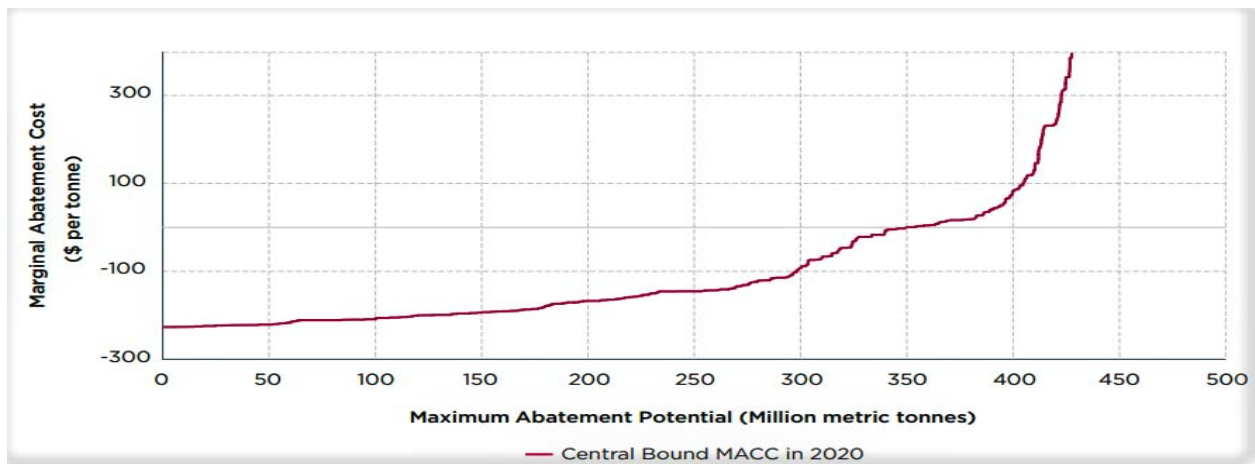


Figure 3: Central estimate of abatement potential in aggregate

Figure 4 further breaks down the reduction potential for the five major ship types. Each ship type, except for passenger ships, can achieve more than a

30% reduction. The lower reduction potential for passenger ships is mainly attributable to the assumption that speed reduction was not an option.

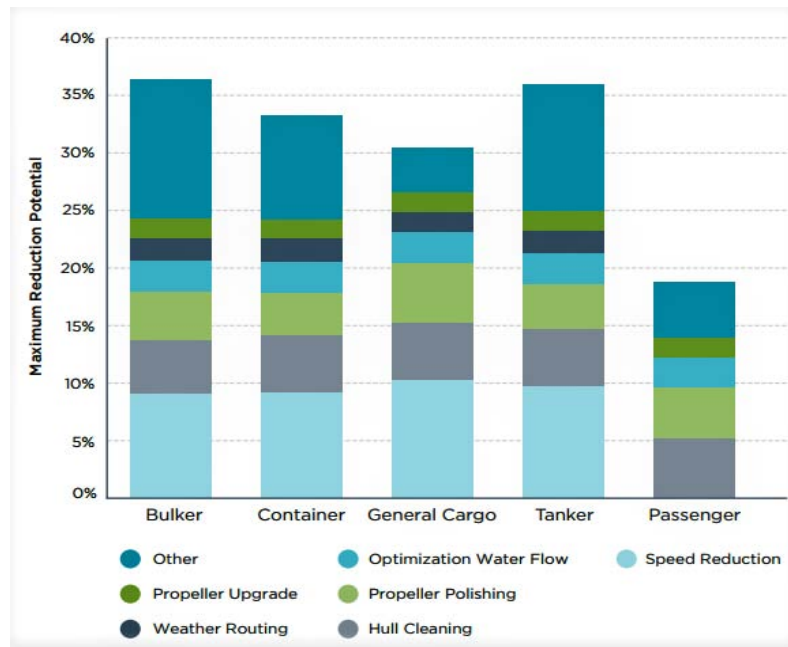


Figure 4: CO₂ reductions of technical and operational measures by ship types

Reorganizing the MAC curve and bundling CO₂ reductions by measure shows the relative cost and reduction potential of each measure.

IV. RESULTS

Mitigation measures on the MAC curves represent the urban sectors of GHG emissions that are compatible with those reported in the city's GHG inventory, and include technologies that reduce electricity and natural gas consumption in buildings, and gasoline and diesel for transportation options. A total of fifty mitigation measures are compiled to represent six

technologies in energy supply (for renewable and non-renewable sources), 36 technologies in residential and commercial/institutional buildings (for space heating, space cooling, water heating, lighting, and appliances, in addition to options to reduce the demand on grid electricity), five measures in passenger vehicles and freight trucks, and three measures for waste from residential and commercial/institutional sources.

This is the classic step-wise MAC curve that has become a fixture of ship-efficiency discussions (Figure 5)

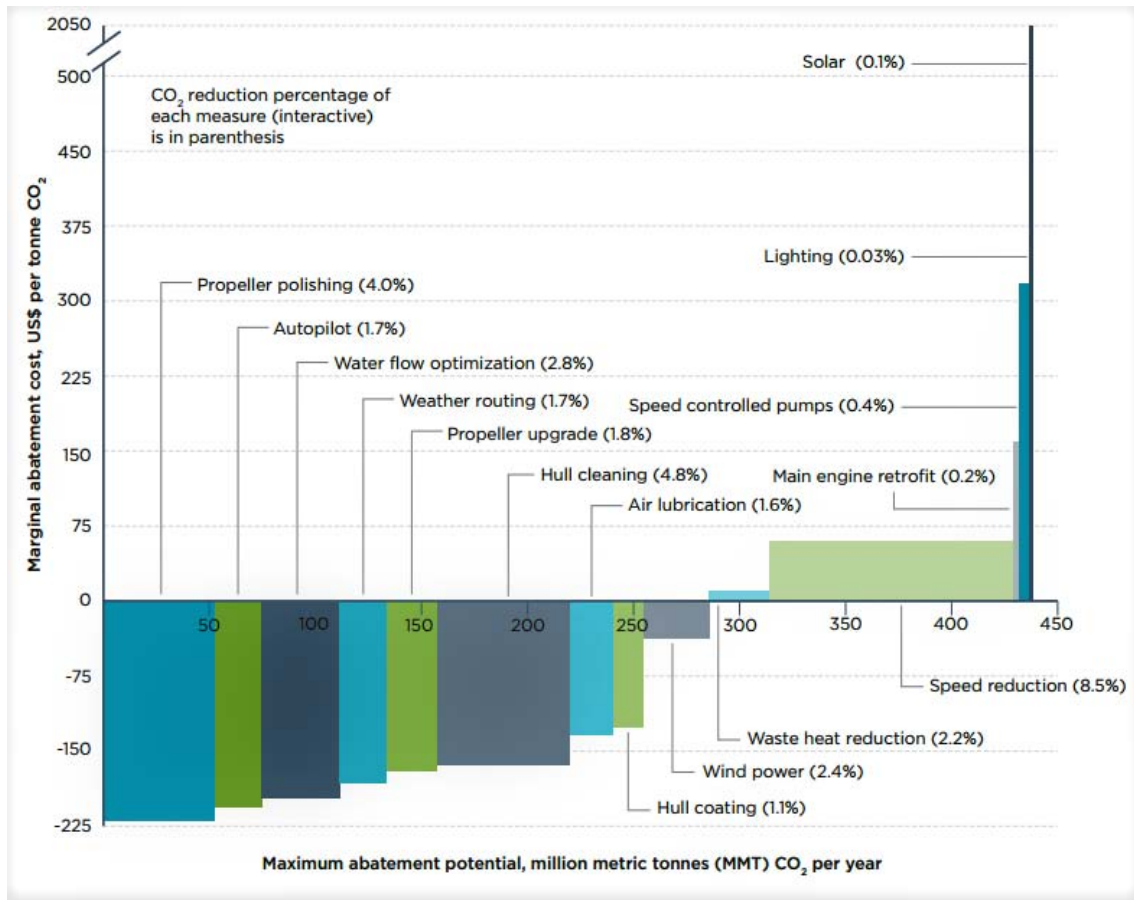


Figure 5: Marginal CO₂ abatement costs of analyzed technologies

Reading from left to right, efficiency measures are arranged according to increasing cost per tonne of CO₂ averted. It was assumed that the measure with the lowest marginal abatement cost would be adopted first, followed by the one with the second lowest MAC, etc. The emission reduction potential of the remaining measures decreases and the cost increases as each additional measure is implemented.

The width of each bar represents the potential of the measure to reduce CO₂ emissions from the world fleet. The height of each bar represents weighted average marginal cost of avoiding one tonne of CO₂ emissions through that measure, assuming that all measures to the left are already applied. Propeller polishing has the lowest average MAC, with moderate CO₂ reduction potential. The total potential reductions apparent in Figure 5 do not line up with those in Figure 3,4 because of the lower resolution required to depict the measures in a stepwise form.

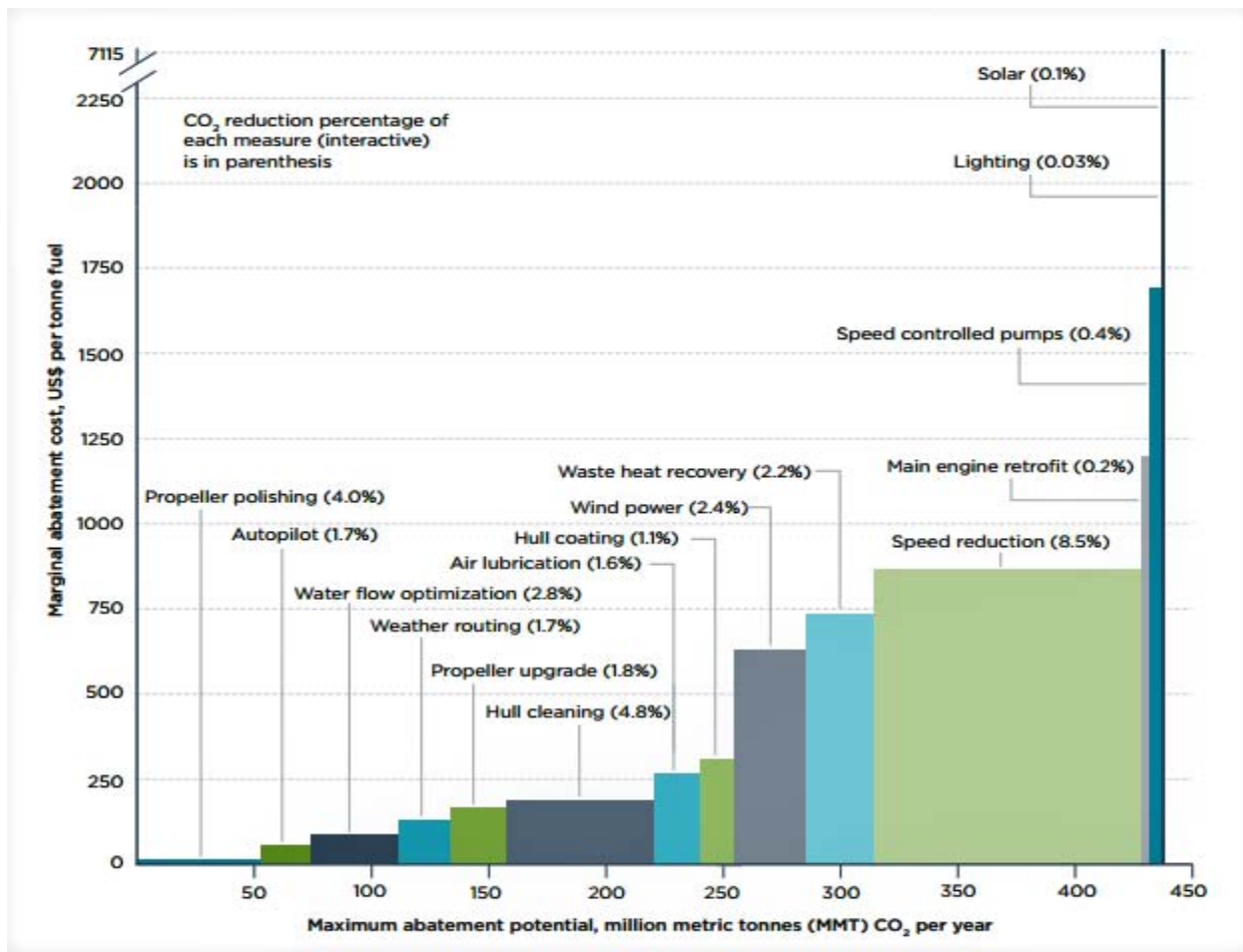


Figure 6: CO₂ emission abatement potential and cost of fuel saving

Figure 6 shows the same step-wise MAC chart as before but with the fuel price removed. As Figure 5, the width of each bar represents the potential of a measure to reduce CO₂ emissions from the world fleet. The difference is that the height of each bar represents weighted average marginal cost of saved fuel. With this visualization, the cost of fuel-saving technologies can be simply compared with fuel price. For example, the cost of saving one tonne of fuel using propeller polishing is \$13, and the CO₂ reduction potential is approximately 50 mmt across the entire fleet. If fuel prices are higher than \$13 per tonne, it makes economical sense to apply propeller polishing.

V. CONCLUSION

Initial efforts to describe the Marginal Abatement Cost (MAC) of ship efficiency measures used relatively broad assumptions. This article summarized here breaks down the fleet in much more detail and focuses on a limited set of available efficiency measures that can be analyzed rigorously. It provides the best policy tool currently available for describing and projecting fleet efficiency potential, but future work can

refine understanding even further, as better performance data for existing and future measures becomes available.

For economic improvements, this study notes many market barriers for technologies that both inhibit deployment of the measures and inject uncertainty into the analysis of benefits. Broadly speaking, these market barriers can be categorized as either split incentives or uncertainty and need to be better elaborated in future MAC studies.

In particular, the issues of split incentives, where the cost of ship efficiency improvements are not directly related to end user benefits, needs dedicated attention. The split incentive concern arises between the vessel owner, who controls capital spending and energy conservation efforts, and the operator, who is responsible for fuel cost. This primarily occurs when vessel especially bulk carriers, tankers, and container ships – are under time charter or bareboat charter. Uncertainty about energy savings is intrinsic and influenced by external factors such as weather, shipping route, etc. Fuel cost, the most important return source from using these measures, is a particularly potent

source of uncertainty when considering efficiency measures.

VI. ACKNOWLEDGEMENT

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Accumulation of Heavy Metal from Sea Water and Sediment on Ghed Area, Gujarat

By Jagdhish Mangukiya , Hetal Parekh & Shuchi Bhatt

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Abstract- The Gulf of Khambhat, is united in a north-south orientation. Bhavnagar district is in Saurashtra region also known as Kathiawad, a part of Gujarat. Geographically the study area lies within the boundaries of Starting point N 21°49' 17.83" E 72°15' 21.03" Ending point 21°49' 46.92" N 72°15' 22.20" E. We have visited seven times during August'14 to February'15. Here we analysed heavy metals from sea water and Sediment.our main object is to prepare baseline study at ghed area.

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GJSFR-E Classification : FOR Code: 100205



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Accumulation of Heavy Metal from Sea Water and Sediment at Ghed Area, Gujarat

Jagdish Mangukiya ^α, Hetal Parekh ^σ & Shuchi Bhatt ^ρ

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I. INTRODUCTION

Heavy metal contamination of the coastal environment continues to attract the attention of environmental researchers due to its increasing input to the coastal waters, especially in the developing countries. Anything that stirs up the water, such as dredging, can resuspend sediments (Abida Begum, Hari Krishna S, Irfanulla Khan, 2009). Ecotoxicologists and environmental scientists use the term "heavy metals" to refer to metals that have caused environmental problems. The metals which have been studied extensively the last decades are: Cd, Hg, Zn, Cu, Ni, Cr, Pb, Co, V, Ti, Fe, Mn, Ag and Sn (Tin). Atmospheric and river inputs, dredging spoil, direct discharges, industrial dumping and sewage sludge are some of the important contributors to metal pollution, which lead to the release of metals to the marine environment (A. Valavanidis & Dr. Thomie Vlachogianni, 2010). As the mangrove forest sediments have a high potential for storing heavy metals from the water in tropical and subtropical regions (Kamaruzzaman et al., 2008; Tam and Wong, 1996; Clark et al., 1998). The high capability of mangrove to absorb and store heavy metals in its sediments is because of the physicochemical properties of these sediments (Qiu et al., 2011; Harbison, 1986).

a) Sea water

Cadmium, copper, lead and zinc salts are usually found in agricultural and industrial liquid waste which discharged into water resources. (McCrea and Fischer 1986 and Qiao-qiao et al 2007). A direct relationship between heavy metal concentrations in

seawater and limpet soft tissues was found in the Vigo estuary area, the levels of Cd and Zn being the ones that showed the greater spatial differences. (M. Perez-Lopez, 2003). The current literature includes some investigation on concentration of heavy metals in sea water in several different coastal areas of the world. One of them was studied in Indonesian. His observation on heavy metals (Hg, Pb, Cd, Cu, Zn and Ni) content in sea water in beaches, were carried out in Jakarta Bay water (Lestari, 2004). Water pollution of heavy metals has become a question of considerable public and scientific concern in the light of the evidence of their toxicity to human health and biological systems (Yayintas et al. 2007a, b; Anazawa et al. 2004; Özmen et al. 2004; Alonsa et al. 2004). The high heavy metal concentration indicated that seawater near the Kepez harbor was so polluted that all living organism may be adversely affected by this pollution. One of the sources of this pollution may be Danube River discharges annually of about 280 tons of cadmium and 4,500 tons of lead, which reach to the seawater of the Dardanells (Süren et al. 2007; Balcı and Türköglu 1993; Turkoğlu et al. 1992; Mee 1992).

b) Sediment

Heavy metal concentrations in surface sediments can provide historical information on heavy metal inputs at that location. Such surface sediment samples are also used as environmental indicators to reflect the current quality of marine systems for many pollutants (Förstner, 1980). Human activity may increase concentration of heavy metals in coastal sediments and at the same time areas of high rural and industrial activity will lead to increase of such sediments in such areas creating high concentrations of pollutants (Luoma, 1983), (Savdeset, et al, 1995). There is a theory that finer sediments contain more heavy metals than coarser ones. The main reason is that smaller grain size particles have a larger surface-to-volume ratio (Salomons, 1984; Martincic, 1990). Zinc, like nickel and copper, shows partial detrital binding. It is impossible to infer bond types for lead and cadmium from the analyses in this study; however, because of the correlation between these two metals, it is assumed that they undergo proportionately similar binding forms. (Perttilä and Brüggman, 1991). Distributions of arsenic (As) and metals in sediments can provide evidence of human activities and their effects on ecosystems and

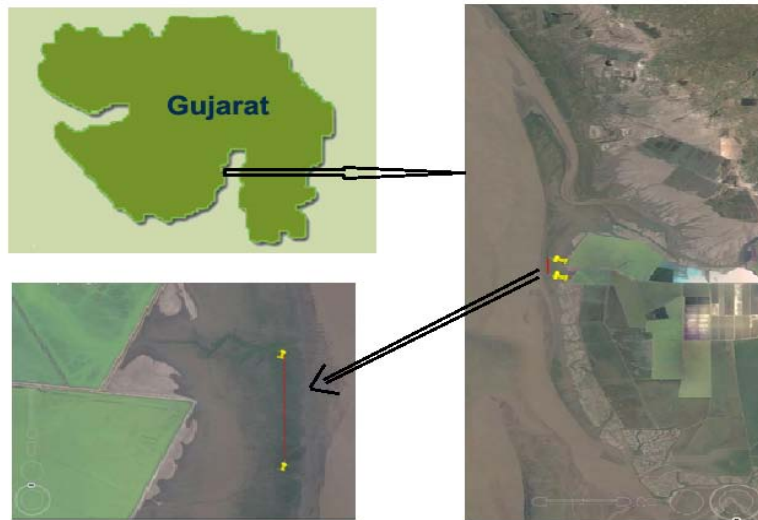
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aid in assessing the risks associated with discharged human waste. Accumulation of arsenic and metals in sediments has implications for local communities, as well as for qualities of river waters (Demirak et al. 2006; Zheng et al. 2008). Accumulation of trace metals occur in upper sediment in aquatic environment by biological and geochemical mechanisms and become toxic to sediment-dwelling organisms and fish, resulting in death, reduced growth, or in impaired reproduction and lower species diversity (Praveena et al., 2007). Pollution will occur from different sources in many ways either from natural or human made. When the pollution was caused by the nature, the effect of pollution is very low and pollution does not persist for a longer duration. (Fractionation of Heavy Metals in Soil of Industrial Area of Mysore City, India, D. Shiva kumar S. Srikantaswamy, 2014).

c) Study Area

Gujarat state is located in the Western part of India. The Gulf of Khambhat, (3,120sq.km) is aligned in a north-south orientation. The Gulf has a distinctive characteristic of having world's highest tidal amplitude of concerning 11m that has potential of production of power and other danger as well. The average precipitation varies from 600mm on the western side to 800mm on the eastern side. However, about 9000km² around the Gulf shows a high concentration of inherent salts in the sediments and ground water has higher salinity reaching 2000ppm and above. Bhavnagar district is in Saurashtra region also known as Kathiawad, a part of Gujarat. Geographically the study area lies within the boundaries of latitudes 21° 49' 17.83" to 21° 49' 46.92" N and longitudes 72° 15' 21.03" to 72° 15' 22.20" E (0.9 km.).



figure

II. MATERIAL AND METHOD

a) Determination of metals in the sea water samples

Analysis of trace metals in sea water was done by APDC-MIBK extraction procedure. The sea water sample were filtered using 0.45 μm millipore filter paper and stored in pre-cleaned, acid washed polyethylene bottle. Samples were acidified with Supra-pure nitric acid or hydrochloric acid to a pH between 2-3. Samples were stored preferably at low temperature to avoid evaporation. Take out 400ml of seawater sample, adjust the pH to 4.0. Add 10ml of 2% APDC solution and shake well for 5min. After 30 sec, add 15 ml of MIBK solvent and shake well for again 20 min. Allow the solution to stand for 15 min for separation. After separation transfer the aqueous layer into a pre-cleaned separating funnel and the MIBK extract into a pre-cleaned 100ml capacity separating funnel. The collected aqueous solution is again extracted by adding 5ml of 2% APDC solution and

10ml MIBK solvent. After separation discard the aqueous layer and collect the MIBK extract into the separating funnel containing the first (MIBK) extract. Extract the metal now by adding 0.1 ml of concentrated nitric acid into the combined MIBK extract, shake well and allow 10min to separate the layers. Add 9.9 ml of Milli-Q water shake vigorously for 5 min and allow the phases to separate. Collect the metal containing acid layer (lower layer) into a 25ml volumetric flask. Repeat the same procedure again and make up to the mark with Milli-Q water. Immediately store in a pre-cleaned plastic bottle and quantify in AAS. For every sample extraction, extract one blank and one standard taking same volume.

Calculation:- Metal concentration (ppm) = AAS reading (ppm) / 16

b) *Determination of metals in the marine sediment samples (total decomposition procedure)*

Sediment samples must be dried before the analysis since the metal concentrations are based on dry weight. The sediment samples soon after collection in the field are immediately air/sun dried and brought back to the laboratory. In the lab they are oven dried at 105°C (60°C in the case of Hg) for a period of 24 hrs and placed in a desiccator until further analysis. The oven dried samples are then powdered using agate mortar to fine powder. The fine sediment powder is then passed through a 250 μ mesh and the collected sediment is subjected to metal analysis by the following procedure. Working standards (100 ppm) of relevant concentrations from stock solutions (1000 ppm) as given below using HNO₃ and UPW (Sigma / E-Merck : AAS standards). Dry powdered sediment is gently heated and digested with Hydrofluoric acid whereby Silica volatilizes as Silicon tetrafluoride. This is followed by treatment with Nitric acid and Perchloric acid to destroy the organic matter. The residue after evaporation of acids is dissolved in 0.1

N HCl and desired metals are determined by Atomic Absorption Spectrophotometry (AAS).

III. RESULT AND DISCUSSION

The Present study was conducted to know the status of heavy metals in seawater and sediments at the coast of Ghed area near Roniyo beyt, Bhavnagar during the study period August'2014 to February'2015. Total 7 visits to the study site were made during the study period. Collection was made according to tide table. Lowest low tide and highest high tide were suitable for the collection. During study Zinc, Selenium, Lead, Manganese, and Cadmium were analyzed from seawater and sediments. Here we noted that throughout study .i.e., From Aug 2014 to Feb 2015 from sea water heavy metals like Zn, Se, Pb, Cd, were 1 ppm observed while Mn values differ all month, not any significant change occurred from sea water samples. In sediment heavy metals like Zinc, Selenium, Lead, Manganese, Cadmium have a 1 ppm there is no variation throughout study.

Table No. 1: Heavy Metal Analysis from Sea water during study period (in ppm)

No	Month	Zn	Se	Pb	Mn	Cd
1	Aug'14	1	1	1	0.93	1
2	Sep'14	1	1	1	8.86	1
3	Oct'14	1	1	1	7.28	1
4	Nov'14	1	1	1	5.46	1
5	Dec'14	1	1	1	3.60	1
6	Jan'15	1	1	1	9.99	1
7	Feb'15	1	1	1	0.1	1

Table No. 2: Heavy Metal Analysis from Sediment during study period (in ppm)

No.	Month	Zn	Se	Pb	Mn	Cd
1	Aug '14	1	1	1	1	1
2	Sep'14	1	1	1	1	1
3	Oct'14	1	1	1	1	1
4	Nov'14	1	1	1	1	1
5	Dec'14	1	1	1	1	1
6	Jan'15	1	1	1	1	1
7	Feb'15	1	1	1	1	1

IV. CONCLUSION

The sample was collected at the coast of Ghed area near Roniyo beyt, Bhavnagar, near Nirma Industry. The variation shows that metals may present in sea water and sediment. Some metals are not detected during study period it shows that the amount of that metals are stable and it's not induced or detected.

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Plant Extracts as an Effective Solution to Mitigate Marine Pollution

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Abstract- Pollution in the marine environment has become a serious problem and the removal of pollutants from the sea has become a topic of great interest to researchers. In this regard, this paper attempts to examine the potential of plant extracts to act as anti-polluting agents of marine environment without degrading its flora and fauna. The present paper focuses on the use of the MSL formula and investigates its efficiency as a natural herder for the reduction of organic matter (including hydrocarbons) in marine waters. Tests for toxicity, Total Petroleum Hydrocarbon (TPH) removal, degradation and dispersant efficiency, as well as microbiological tests, were performed using the MSL product as the plant extract based formula (made up of 89 percent plant extract solution, 3 percent hydrogen peroxide and 8 per cent of Isopropyl alcohol).

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Plant Extracts as an Effective Solution to Mitigate Marine Pollution

Kaniklides Stavros ^α & Costas N. Costa ^σ

Abstract- Pollution in the marine environment has become a serious problem and the removal of pollutants from the sea has become a topic of great interest to researchers. In this regard, this paper attempts to examine the potential of plant extracts to act as anti-polluting agents of marine environment without degrading its flora and fauna. The present paper focuses on the use of the MSL formula and investigates its efficiency as a natural herder for the reduction of organic matter (including hydrocarbons) in marine waters. Tests for toxicity, Total Petroleum Hydrocarbon (TPH) removal, degradation and dispersant efficiency, as well as microbiological tests, were performed using the MSL product as the plant extract based formula (made up of 89 per cent plant extract solution, 3 percent hydrogen peroxide and 8 per cent of Isopropyl alcohol). Furthermore, four different parameters such as COD, BOD, TPH and FOG were analyzed in order to determine the effectiveness of the MSL formula. The present study has determined that the safe administration of the product will not affect aquatic life and hence this plant extract based formula will not function/ behave as a polluting agent. The effectiveness of the MSL product was studied on site against different organic compounds by monitoring its activity and effects in the context of the Ayia Napa Port Project. Consequently, biodegradation test indicated that the maximum degradation rate of the mixture of the MSL and Arabian crude oil was 90.48 % after 96 hours of activity. The results demonstrate that plant extract formulas such as the MSL formula have the potential to act as eco-friendly, biodegradable, non-toxic, and cost-effective alternatives to be utilized in restoration strategies and clean up operations in marine environments.

I. INTRODUCTION

Industrialization as a mainstream basis for human development into new environments and habitats has resulted in an increasing rate of pollution wherein the marine ecosystem is being continuously subjected to the harmful effects of human activity. Both sea-based and off-shore based industrial operations have been contributing to marine pollution (Todd, Ong, & Chou, 2010). Among the various activities that contribute to marine pollution include oil and fuel spills from ship engines, run offs containing organic materials, disposal of construction materials containing solvents and paints, and accidents such as boat sinkings or sewage disposals (Fartoosi, 2013). The effects of these pollutants include the accumulation of organic and

inorganic materials in the ocean, oil sedimentation, reduction of UV disinfection, increasing levels of water toxicity, algae and bacterial blooms, and fouldors (Tornero & Hanke, 2016). The main impact of pollution in marine environments is the disruption of the entire marine life and marine biodiversity (Derraik, 2002). Crude oil spills are one of the most hazardous pollutants for the marine ecosystem, thus considerable resources have been expended in efforts to try and limit their impact. One way to clean such spills is through the use of a special type of amphiphile known as chemical herder which is sprayed to the surface of the water where oil is spilled (Athas et al., 2014). Over the years, amphiphiles from plant extracts have been gathering more attention. The mechanism through which plant extracts work as anti-pollutant agents in water column is a topic that warrants further investigation. The pollution of water bodies such as lakes, rivers, ports etc. can be addressed through various ways such as reducing the surface tension of water to allow the spills to extend over a region for easy evaporation or increasing the forces of adhesion of the pollutants to make them come together either for the ease of burning or collecting of the waste material (Gunde, Dawes, Hartland, & Koch, 1992; Sridhar & Rami Reddy, 1984). As a result, reverse engineering is needed to understand how plant extracts work as antipollution solutions in water bodies. This paper provides an extensive discussion of plant extracts as an antipollution solution in water column by presenting the mechanism through which these extracts achieve their antipollution effects; furthermore, acceptance of their use as a dispersant is examined under the EPA Regulatory Protocol guidelines (Environmental Protection Agency, 2017). This paper focuses specifically on MSL, a plant extract based formula, and discusses its efficiency in the dispersion of oil spills in water column and the oil biodegradation rate upon treatment with the formula. Several advantages of the use of the MSL product as a plant extract alternative to the commercially available chemical dispersants have also been identified and are discussed in the paper.

II. REVIEW OF LITERATURE

The use of dispersants is increasing worldwide and guidelines are readily available for their substantial use in industrial settings (ExxonMobil Research and Engineering Company, 2008). However, their use in natural environments such as the aquatic ecosystem is

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controversial as these dispersants also have potential drawbacks. Most dispersants used in the sea do not exhibit significant levels of toxicity. Measured levels are on par with the toxicity observed in shampoos and household liquid dish wash solutions (Word, Clark, & Word, 2015). However, these dispersants are chemicals and when added to an area that has been negatively impacted due to oil spills only serves to further increase the levels of pollution in the affected area. Furthermore, when an oil slick is dispersed, it further mixes toxic substances into the water thereby becoming hazardous to living organisms (Prince, 2015). Hence, the need persists to develop natural dispersants that could potentially be used as dispersants without harming marine environments.

Plant extracts have been used over the years in water purification applications and schemes. Some studies have claimed that the coagulation properties of plant extracts such as *M. oleifera* make them suitable for the treatment of wastewater (Ghebremichael, 2004). Studies have also focused on the use of plant extracts for treating surface water (Jahn, 1986; Sanghi, Bhattacharya, Dixit, & Singh, 2006). Das and Chandran (2011) presented an updated overview of the petroleum hydrocarbon degradation by microorganisms under different ecosystems. Chachere (2012) reported on a team of USF researchers who demonstrated that the mucilage from prickly pear cactus also works as a natural, non-toxic dispersant for oil spills. The USF group, led by chemical engineering professor Norma Alcantar, carried out research to identify effective alternatives to chemical dispersants. According to the study, unlike chemical dispersants, cactus mucilage is non-toxic and is harmless to the marine environment.

Guo et al. (2014) aimed at utilizing a natural dispersant that was extracted from a cactus plant native to Mexico to form oil-in-water emulsions. In this process, the natural biomaterials extracted from the cactus plant are responsible for causing the dispersion of the oil phase into the water. The use of plant extracts as anti-pollutant solution in the water column was elaborated in detail by Gupta et al. (2015). The plant extract, phytol, is also biodegradable in the marine environment (Ramlagan, 2017). According to Gupta et al. (2015), phytol has an allylic bond next to the ester functional group which facilitates the hydrolysis of the amphiphile and as a result releases a highly water-soluble cationic group into the water column where it is readily diluted.

Zeiger et al. (2016) further recognized that the common cleanup methods for oil spills still have challenges due to the chemicals used, as these chemicals absorb large amounts of water in addition to the oil itself, thus rendering the entire process less effective. They further identified two aquatic plants, *Salviniamolesta* and *Pistiastratiotes*, which possess special characteristics due to their trichome-covered surface that repels water. This characteristic of the

plants is a result of their hydrophobic surface chemistry and hierarchical micro and nano scale surface structure. Hydrophobic surface chemicals such as wax protect the plant from excessive evaporation of water, mechanical damage and degradation by water (Zeiger et al., 2016). An experiment was conducted by O'Brien and Tobin (2016) at the National Science Foundation to determine the effect of sunlight on oil spillage in a marine environment. According to the study, when the oil is exposed to excessive sunlight, light energy initiates or catalyzes certain chemical reactions that convert the spilled liquid oil into sludge. This sludge then inhibits the process of oil degradation. Consequently, as a result of this experiment, the researchers were able to come up with models that could assist with the design of optimum cleanup strategies for the marine environment (O'Brien & Tobin, 2016).

Choi & Cloud (1992) investigated the use of natural sorbents for the cleanup of oil spills and more specifically, tested the efficiency of milkweed (*Asclepias*) to remove spilled oil. However, treatment by alkali scouring agents reduces the oil sorption capacity of milkweed and cotton fiber significantly. It was further shown that with appropriate mechanical equipment, the recovery of absorbed crude oil from milkweed and cotton can be facilitated wherein the fiber can be reused several times during the cleanup. The results of the research demonstrate that partial or total commercial synthetic oil sorbent substitution using natural sorbent materials is advantageous for oil spill cleanup operations.

Some of the more commonly used chemical herders are silicone polyethers (identified as SilsurfA108 and Silsurf A004-D)(Ottawa, 2012). However, these chemical herders are not biodegradable and will persist in the marine environment even long after the oil has been burnt in situ. These chemical herders have high levels of water toxicity contributing to increased secondary adverse impacts to the marine life (Lassen, Hansen, Mikkelsen, & Maag, 2005). Green herding is an alternative to chemical herding as green herders are degradable and exhibit reduced levels of water toxicity compared to chemical herders (Wanger sky, 1982).

The role of dispersants is not only to mix small droplets with water and allow the natural degradation and microbial action to take place more efficiently, but to also disperse the oil in an extended area so as to facilitate faster evaporation of the oil. When the oil-water tensile force is reduced, the polluting oil is allowed to spread within a broad area, which exposes more of the oil to direct sunlight as well as increases the surface-volume ratio to evaporate the oil naturally. The spreading of oil over a large section of a marine environment also means that the harmful effects of the oil spill are felt not just in a single region but are spread across an expansive region, thereby minimizing their effectiveness (Allen, 1984).

Another identified method for cleaning up marine environments is phytoremediation, or phytoextraction (Zalewsk & Nogalska, 2014). These methods involve a number of processes that utilize plants for the uptake, storage and degrading of contaminants within the plant tissues. Yet another process uses disphytostimulation or rhizodegradation, which utilizes hizospheric associations between the plants and symbiotic microbes to degrade the oil spills (Oh, Cao, Li, & Cheng, 2014). Phytovolatilization, based on the ability of plants to uptake pollutants from the growth matrix, which subsequently transforms and volatilizes the pollutants to the atmosphere, has also been used in marine environments (Limmer & Burken, 2016).

When the oil is spilled in seawater, one way to clean it up is through absorption of the oil, leaving the seawater intact. In such cases, plant extracts have been used to absorb oil pollutants from the marine environment. The most common materials used include sawdust and other aquatic plants. A major shortcoming of these traditional materials is that they absorb both oil and water and thus are less effective in selectively removing the oil from a water environment. With this in mind, researchers have investigated plants that can potentially repel water (super hydrophobic) and at the same time attract oil (super oleophilic). These materials could theoretically achieve selective absorption of oil. Two plant materials that have been identified and isolated for such a purpose are *Salviniamolesta* and *Pistiastratiotes*. These plants have certain structural characteristics that allow them to repel water and attract oil (Zeiger et al., 2016). The advantage of these materials is that they do not have any negative impact on the aquatic life. They are biodegradable and can be processed by microbes if traces of their residues remain in the marine environment. The selective absorption properties of these materials imply that they do not interfere with seawater either, however, they cannot be effective in cases of large spills especially when oil spills occur in the deep seas. Research studies have also attempted to investigate whether plant extracts could act as anti-pollutants in marine environments through chemical action, in cases where plant materials have been utilized to achieve the cleanup, usually in small-scale oil spillage incidents. And although plant extract based amphiphiles are biodegradable, they might prove hazardous to marine life, hence, there is a need to carefully examine levels of toxicity when using such extracts. In this regard, the MSL solution, which is a plant extract formulation and is the focus of the present study, is investigated in terms of its cleanup efficiency, toxicity and bio-degradability.

III. METHODS

Having thoroughly examined and extensively explained the advantages of natural herders, the present paper has focused on exploring the use of the MSL formula and investigating its efficiency as a natural herder for the reduction of organic matter (including hydrocarbons) in marine waters. Absorbance measurements have been used to assess concentrations of crude oil using the UV/V spectrophotometer and demonstrate the efficiency of MSL as a dispersant. MSL is used as the plant extract formula, which is made up of 89 per cent plant extract solution, 3 per cent hydrogen peroxide and 8 per cent Isopropyl alcohol. Several tests have been conducted to understand the efficiency, mechanism of action and degradation capabilities of the MSL product. The research study was designed to determine the efficiency of the natural herders wherein degradation tests for the known oil dispersant were also conducted. Furthermore, toxicity studies were undertaken to examine the optimum concentration of the formula in seawater.

a) *Efficiency and degradation tests*

For the determination of the efficiency index of the MSL formula, Appendix A to WSL Report LR 448 (OP) was used to guide the experiment. This is a guideline specification that relates to procedures for applying oil spill dispersants at sea or on beaches and is prepared in compliance with UK recommendations before any dispersant can be recommended for use.

Effectiveness assessment is important for a dispersant to attain the global standards and for the marketability of the product. Firstly, the efficiency test of the sample of MSL as a dispersant was performed. In the preparation of dispersed oil, the stock of dispersed oil was prepared by adding 5 ml of crude oil to natural seawater. The mixture was prepared in the ratio of 1:10 for MSL and crude oil respectively. The mixture was shaken vigorously for 10 minutes. The absorbance reading was taken for different concentrations of crude oil using a UV spectrometer at 580 nm. The calibration curve for absorbance versus different concentrations of crude oil was plotted. In order to determine the effectiveness as a dispersant, the following formula was used:

$$\text{Efficacy \%} = \frac{(\text{Final weight (g) of crude oil} \times 100)}{(\text{initial weight (g) of crude oil})}$$

In addition, bio-degradation tests were conducted with the sample solution of the MSL formula. The degradation test was conducted for 96 hours. After the data was tabulated (Table 1), the curve of the residual concentration mix against the time taken for observation of the rate of biodegradation was plotted (Fig. 1).

b) *Toxicity tests*

The toxicity tests were conducted under three different test conditions where natural phytoplankton, shrimp and fish were mixed with the MSL product. The formula was first tested in natural zooplankton population (Table 2), then in shrimp population (Table 3) and then in fish (Table 4) wherein the test conditions included salinity of 39 per cent, temperature of 23 – 24 °C and pH of 7.5- 8. The concentration of the MSL solution was increased from 25 to 400 ppm wherein a Chi2 test was used to examine whether a best fit was acquired.

c) *Total Petroleum Hydrocarbon (TPH) removal tests*

Tests were performed to examine the efficiency of the MSL plant extract formulation in reducing hydrocarbons in the coastal waters of the city of Limassol wherein the MSL product was sprayed to the surface of the seawater using a specially equipped boat. It was observed that the entire dispersion process of the MSL formula, from the addition to the water column of the marine environment to the end of the biodegradation phase, occurs in five stages. In stage one, the oil spill is black in color at the surface of water column with some oil stuck to the sediments in the marine environment. In stage two, the solution turns brown when the MSL formula has acted on the oil and the evaporation is at its initial stage. In stage 3, the solution is light brown in color and there is moderate evaporation and biodegradation. In stage 4, a sheen solution is formed and the pollutant has started to clear at the end of the evaporation process. Finally, the marine environment is clean and there is adequate ventilation of the water and the aquatic life can thrive without being affected by any toxicity in the marine environment. Samples of seawater were taken 2 hours after spraying the formulation. The treatment with the MSL product was carried out by spraying the formula in a specific route twice in a 2-week span at a distance of about 200 meters from the coastline. The points for analysis were taken from the Old Port to the Crown Plaza Hotel in Limassol.

d) *Microbiological tests*

Microbiological tests were performed in the same region specified in the previous section (Limassol coast line). Enterobacter, E. coli, and Enterococcus colonies were examined in 100 ml seawater samples taken during the same 2-week span. The values of colonies per 100 ml were checked both before and after treatment

e) *Test of other contaminant parameters*

Several tests were carried out in marine locations to determine the effectiveness of the MSL formula on different contaminant parameters: biological oxygen demand (BOD), chemical oxygen demand (COD), total petroleum hydrocarbons (TPH), and Fats oils and Grease (FOG). TP (Total Phosphorous) and TKN

(Total Kjeldahl Nitrogen) were also tested as additional parameters.

IV. RESULTS AND DISCUSSION

In the process of cleanup and dispersion of oil spills in the marine environment, the MSL formula works through a mechanism of action, the effectiveness of which is based on the high surface tension process. MSL acts to change the surface tension of the water column relative to that of the oil spills and consequently affects the interaction of the two liquid molecules. Marine environment pollutants such as oil spills and other organic compounds are composed of hydrocarbon compounds. When these organic compounds come into contact with the MSL formula, a significant surface tension reaction is initiated. This results in organic components taking the maximum surface area on the surface of water. The larger surface area of the oil implies that the rate of evaporation of these pollutants will increase and thus the degradation rate will also increase. When the MSL formula comes into contact with the organic compounds, the cohesive forces within the molecules are significantly reduced. As a result, the surface tension of the water in relation to oil, or the oil-water interface force is greatly reduced, resulting in the oil molecules spreading on the surface of water column. The oil is also broken down into tiny droplets of oil that spread over a large surface area, and through the action of solar rays, the oil evaporates at a faster than normal rate. Another way through which the MSL process facilitates the marine environment cleanup process is through the breaking down, by microbes, of the small droplets of oil created after the dispersion action, resulting in an accelerated rate of natural degradation. The evaporation and the natural degradation of the oil spill result in an immediate reduction in the concentration of the oil- MSL mix, as is the case with organic oil solutions such as Arabian crude oil. In the case of organic sediments such as TPH (Total Petroleum Hydrocarbons), the actions of the MSL formula at the early stage should convert the organic sediments to liquid form, and then facilitate their dispersion and evaporation.

Thus, it is imperative to examine the efficiency, bio-degradation capability and the toxicity properties of the MSL formula, which is important for examining its safety and efficiency in real world scenarios.

In order to calculate the efficiency of the sample that was used in the laboratory, the formula for efficiency was used:

$$\text{Effectiveness (\%)} = \text{Total oil dispersed} \times 100 / (\ell_{\text{oil}} V_{\text{oil}})$$

$$\begin{aligned} \text{Effectiveness (\%)} &= \text{Final weight (g) of crude oil} \times \\ &100 / \text{initial weight (g) of crude oil} \\ &= 3.99 \times 100 / 4.62 \\ &= 86.36\% \end{aligned}$$

The next procedure involved the biodegradation test of the sample solution of the MSL formula. The degradation test was conducted for 96 hours and the following table was prepared.

Table 1: Results of degradation test

Time (hr)	Abs*Dil	Residual Concentration (ppm)	Degradation (%/day)	Cumulative degradation (%)
0	0.420	4740.00	0.00	0.00
24	0.230	2595.71	45.24	45.24
48	0.090	1015.71	33.33	78.57
72	0.060	677.14	7.14	85.71
96	0.040	451.43	4.76	90.48

After the data was tabulated, the curve of the residual concentration mix against the time taken for observation of the rate of biodegradation was plotted in Figure 3.

When the experiment was conducted to determine the efficiency of the MSL as the plant extract formula using Arabian crude oil as the oil spill in a water column, the test indicated that the MSL is efficient when used as a crude oil anti-pollutant or used in any dispersant capacity. The efficiency of the MSL was found to be 86.36%. This was found to be far greater than the 60% efficiency for a dispersant which is recommended by EPA 1993. This means that when the

MSL is used in the cleanup of marine environment after an oil spill has occurred, it will remove at least 86% of the crude oil that has spilled into the sea.

The biodegradation test indicated that the maximum degradation rate of the mixture of the MSL and the Arabian crude oil was 90.48 % after 96 hours. This corresponded to 72.38% of the initial concentration of 4740mg/L (ppm). The finding demonstrated that the rate of MSL biodegradation is high during the oil spill cleanup process. This rate of degradation means that when MSL is used in the case of an oil spill, after 96 hours over 90% of the oil and MSL mixture will be degraded.

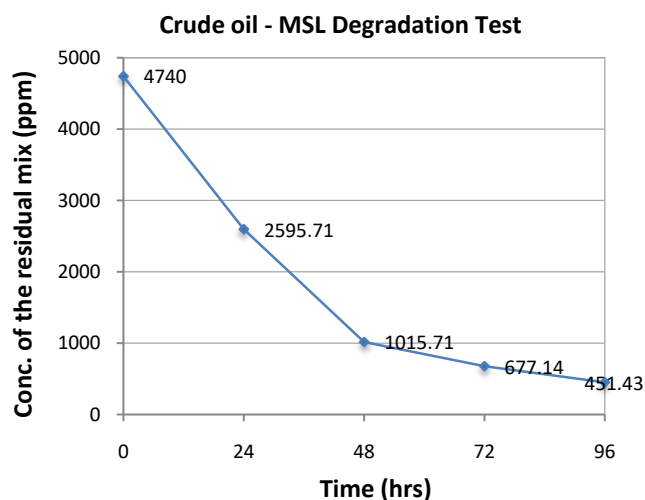


Figure 1: Biodegradation test for mix of crude oil and MSL after 96 hr.

For the toxicity tests, the MSL formula was first tested in the natural zooplankton population wherein the test conditions included salinity of 39 per cent, temperature of 23 – 24 °C, pH of 7.5- 8 and with *Chlorella salina* as the predominant organism. The concentration of the MSL solution was increased from 25 to 400 ppm wherein a Chi2 test was used to examine whether a best fit was acquired. The results of the toxicity tests in natural phytoplankton population revealed that the average number of cells was reduced significantly

wherein with (n-2) degrees of freedom (9-2=7), a critical Chi2 value of 2.167 was acquired (which is less than the total Chi2 of 35.08, see Table 3).

Table 2: Toxicity tests with natural phytoplankton population

No.	Concent ration (ppm)	Average of cells x 10 ⁶ / ml after 96 h	% reduction compared to control	Chi2 test
1	Control	19.4	0	0.00
2	25	17.7	8.8	0.37
3	50	16.4	15.4	1.14
4	100	16.3	20.6	1.21
5	150	15.0	23	2.45
6	200	15.1	22	2.34
7	250	14.3	26	3.29
8	300	11.8	39	7.30
9	400	7.8	59	17.00
Total Chi2				35.08

The MSL is then tested in seawater containing shrimp population wherein the test conditions included salinity of 39 per cent, temperature of 23 – 24 °C, pH of 7.5- 8 and with *Palaemon serratus* as the predominant organism. The concentration of the MSL solution was increased from 50 to 600 ppm wherein a Chi2 test was used to examine whether a best fit was acquired. The

results of the toxicity tests in the shrimp population demonstrated that the average number of cells was reduced significantly after 96 hours wherein with (n-2) degrees of freedom (12-2=10), a critical Chi2 value of 3.94 was acquired, which was less than the total Chi2 at 48.00 (Table 4).

Table 3: Toxicity tests with Shrimp

No.	Concentration (ppm)	%observed mortality	Chi2 test
1	Control	0	2.00
2	50	0	2.00
3	100	0	2.00
4	150	0	2.00
5	200	0	2.00
6	250	0	2.00
7	300	0	2.00
8	350	10	10
9	400	10	10
10	500	30	30
11	550	60	60
12	600	90	90
Total Chi2			48.00

The MSL formula was then tested in seawater with fish population wherein the test conditions included salinity of 39 per cent, temperature of 23 – 24 °C, pH of 7.5- 8 and with *Mugil cephalus* as the predominant organism. The concentration of the MSL solution was increased from 50 to 600 ppm wherein a Chi2 test was used to examine whether a best fit was acquired. The results of the toxicity tests on the fish population revealed that the average number of cells was reduced significantly after 96 hours wherein with (n-2) degrees of

freedom (12-2=10), a critical Chi2 value of 3.94 was acquired, which was less than the total Chi2 at 48.55 (Table 5).

Table 4: Toxicity tests with fish

No.	Concentration (ppm)	%observed mortality	Chi2 test
1	Control	0	3.80
2	50	0	3.80
3	100	0	3.80
4	150	0	3.80
5	200	0	3.80
6	250	10	2.06
7	300	10	2.06
8	350	30	0.17
9	400	50	0.38
10	500	80	4.64
11	550	100	10.12
12	600	100	10.12
Total Chi2			48.55

The entire dispersion process of the MSL formula from the addition to the water column in the marine environment to the end of the biodegradation stage occurs in five states. In stage one, the oil spill is black in color at the surface of water column with some stuck at the sediments in the marine environment. In stage two, the solution turns brown when the MSL product has acted on it and the evaporation is at its initial stage. In stage 3, the solution is light brown in color and there is moderate evaporation and biodegradation. In stage 4, a sheen solution is formed and the pollutant has started to clear at the end of the evaporation process. Finally, the marine environment is clean and there is adequate aeration of the water and the aquatic life and thrive again without being affected by the possible toxicity of the environment. This process is shown in Figure 2.

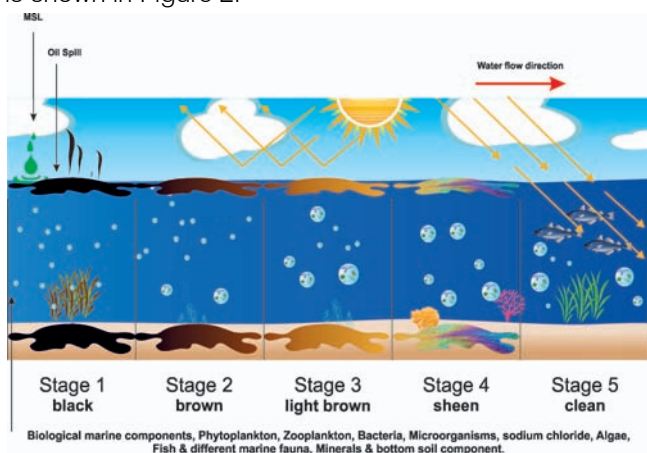


Figure 2: Mechanism of action of MSL on oil spills in the marine environment

An EPA supervised test to assess reduction of the Total Petroleum Hydrocarbons (TPH) on the marine sediments in the Larnaca Marina showed similar results to the reduction rate observed in this experiment. The initial concentration of the TPH given in mg/kg was tested at various dates between June and December of 2016. The initial concentration of the TPH was at

1191.00 mg/kg, and at the end of the test period (6 months) the TPH concentration was at 54.10 mg/kg. This represented a remarkable 95% reduction in the concentration of TPH. The curve drawn for the concentration (mg/kg) against time in sampling dates, showed a similar negative slope as the one shown for the MSL action on the Arabian crude oil. However, the difference in the time taken for the reduction in the TPH concentration in the two cases could be attributed to the different levels of starting concentrations used for the Arabian crude oil and the TPH. The higher percentage decrease in the concentration of the TPH can be attributed to the longer time of test compared to only 96 hours that was used for the MSL action on the Arabian crude oil. The curve that was obtained for the Larnaca test is shown in Figure 3.

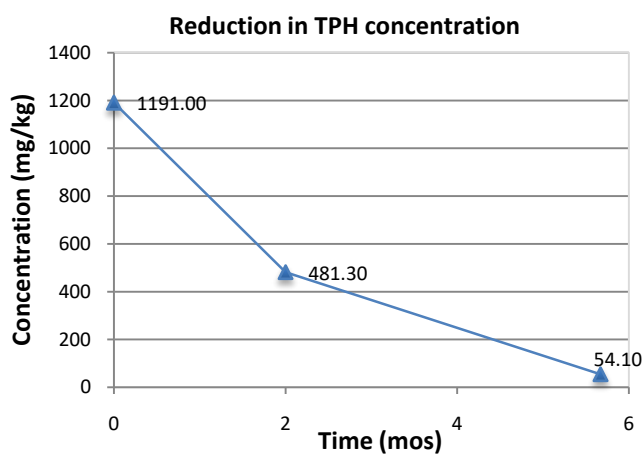


Figure 3: Reduction of TPH concentration using the MSL formula at the Larnaca Marina

The MSL formula has further advantages such as efficiency for cleaning up both the organic compounds deposited on the surface of water column and those that are deposited on sediments in the marine environment. This ensures that all traces of organic compounds that have adverse impacts on the marine environment degrade completely. This is

especially important in the case of pollution that occurs when organic compounds are washed down from higher grounds through surface run-off and rest on sediments on the beaches of water bodies. The action of the MSL formula ensures that all the pollutant traces and the dispersant traces are cleaned up thoroughly after the application. This is possible because MSL is biodegradable unlike chemical dispersants, traces of which can be found in the marine environment after they have carried out their dispersion function. This can be attributed to the fact that chemical dispersants are not biodegradable while their efficiency is below that of MSL meaning traces of the organic compounds they are meant to clean up will still be present in measurable

quantities in the marine environment. After the application of the MSL formula, oil molecules are broken down into tiny droplets most of which evaporate easily while the remaining are degraded by the microbes in the marine environment. The use of MSL leaves the marine environment in the state prior to the use of the formula and it may even clean other pollutants that are present even before the oil spillage incident occurs. In order to illustrate the clean up capabilities of the MSL formula, images of the Nissi Beach in Ayia Napa, Cyprus, before and after the use of the product are shown in Figures 4 (a) and (b). This effect was achieved within a 7-day treatment period in July 2016.

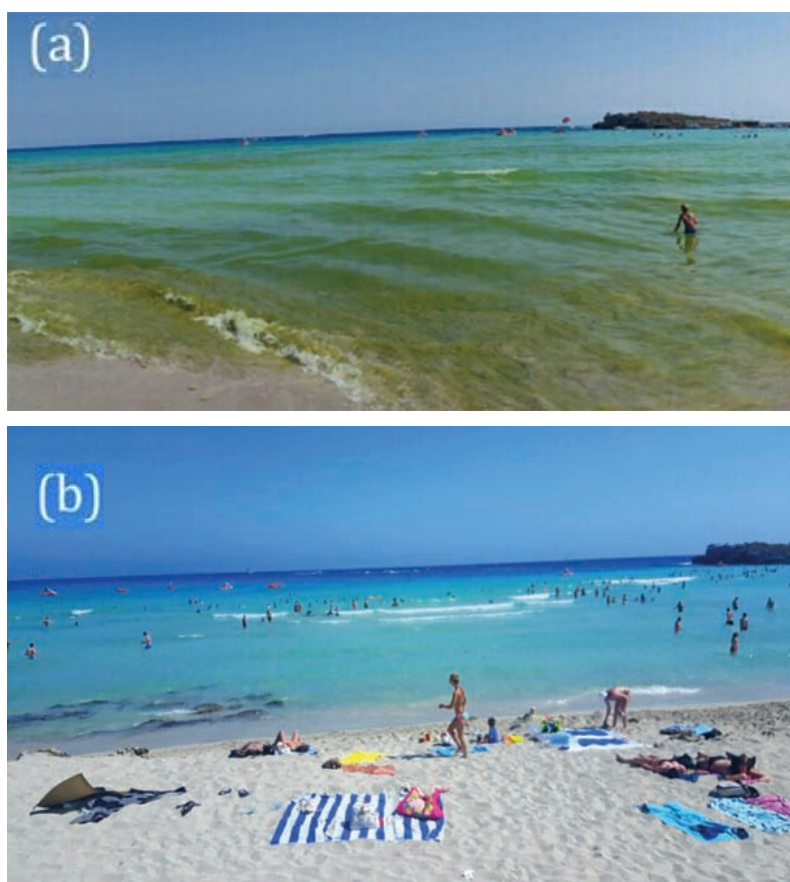


Figure 4: Nissi Beach (a) before and (b) after treatment with the MSL formula

Furthermore, the present study examined the application of the MSL formula on the coastline of Limassol, which revealed a significant reduction in the concentration of TPH in the seawater samples tested (Figure 5). In addition, significant reduction in the Enterobacter, E.coli, and Enterococcus colonies was observed in the samples of water taken twice during the 2-week span of the treatment (Figures 6-8). The MSL formula can be applied in an open marine environment where it is exposed to sunlight and the action of microbes that can facilitate the process of degradation. The product can also be applied to different concentrations of oil spills depending on the type of

crude oil and, in this case, there are other factors that affect the process of dispersion. Seawater salinity, waves and water currents, exposure to sunlight, concentration of microbes, and concentration of pollutants are highly likely to affect the process. Sunlight is the first factor that affects the rate of dispersion. After organic compounds are spread on the surface of water, the intensity of sunlight then determines the rate of biodegradation through evaporation. In the case where there is intense solar radiation, the evaporation process takes place rapidly, which implies that the degradation will take place faster. Thus, the MSL formula is more efficient in intense sunlight.

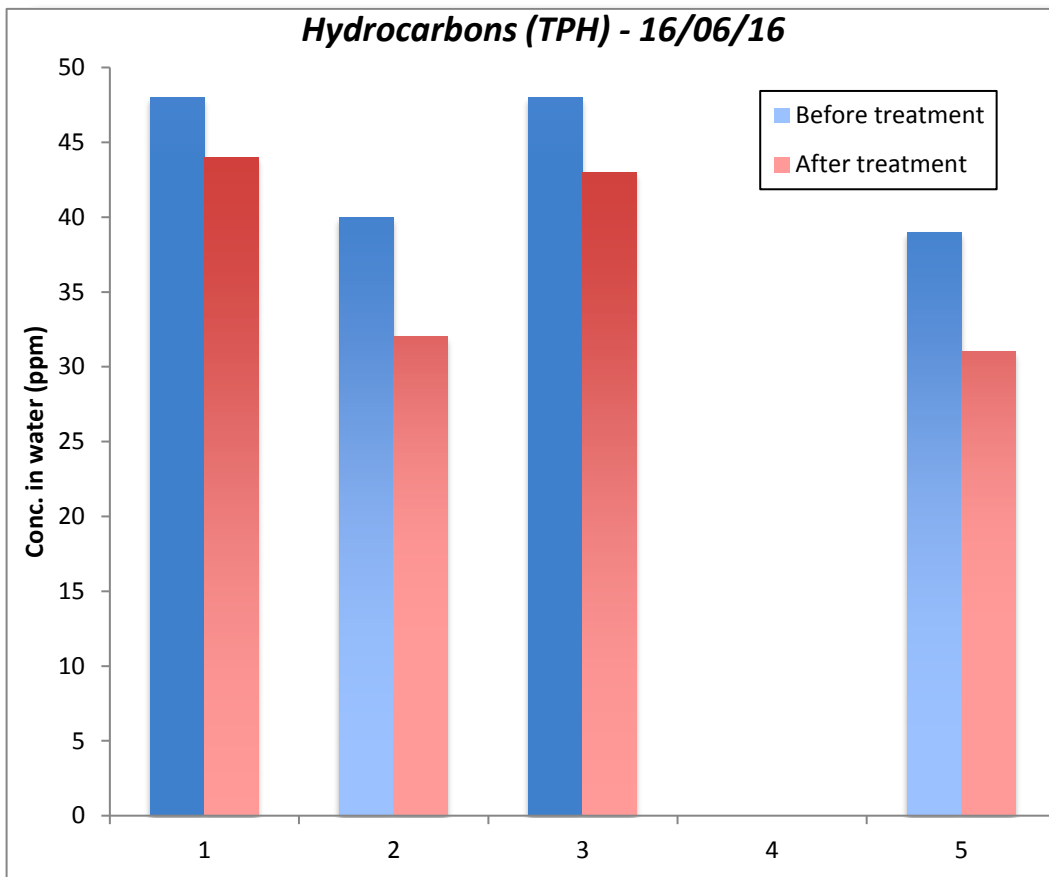
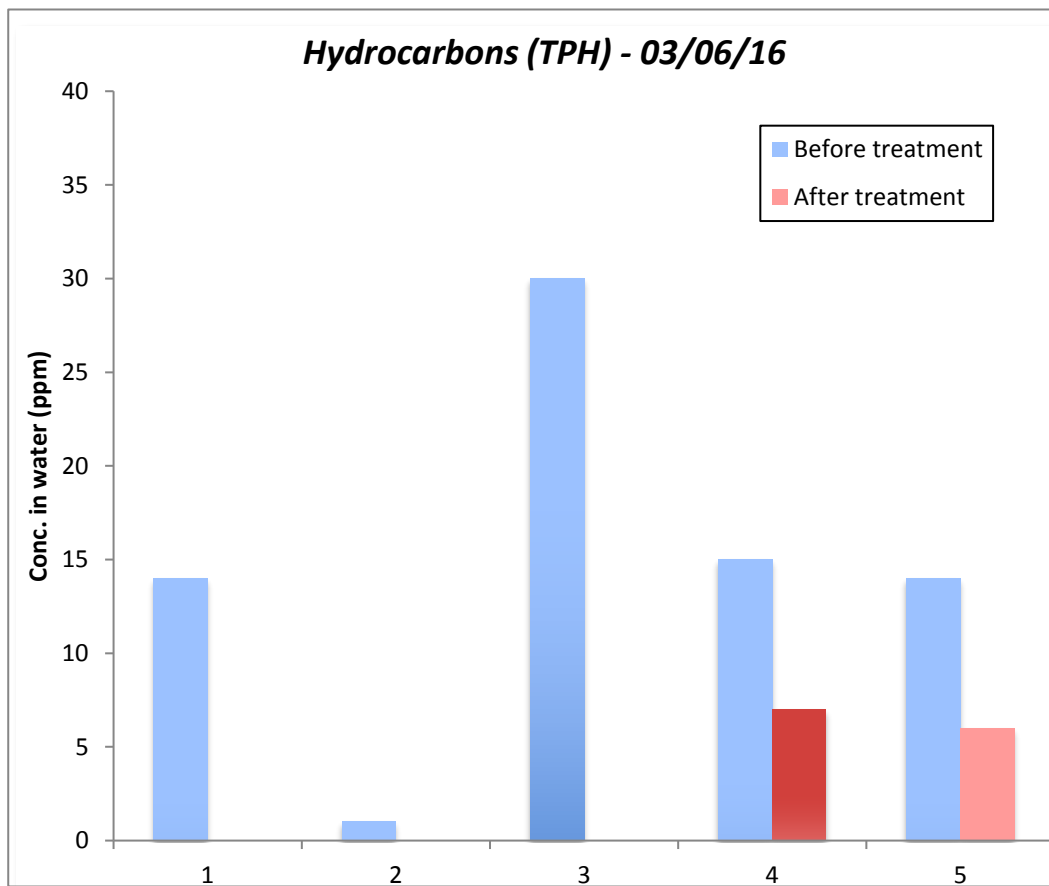


Figure 5: Analysis Results (TPH)

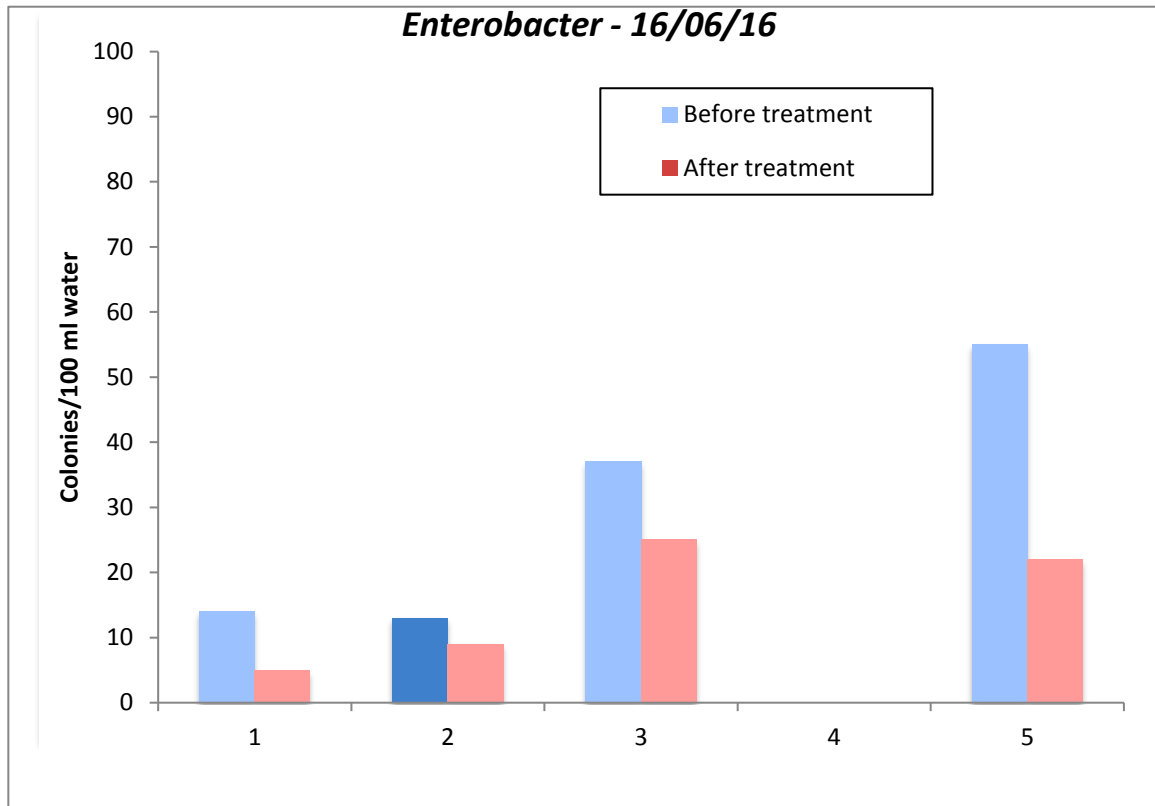
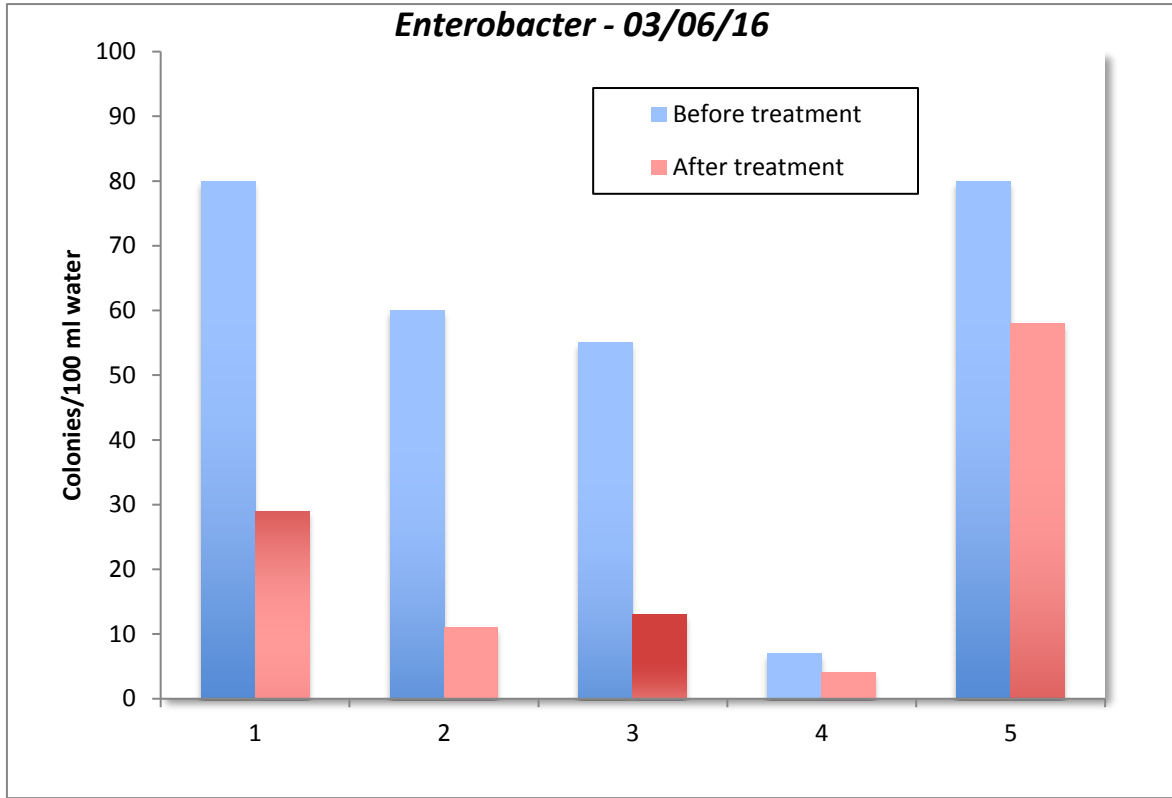


Figure 6: Microbiological tests (Enterobacter)

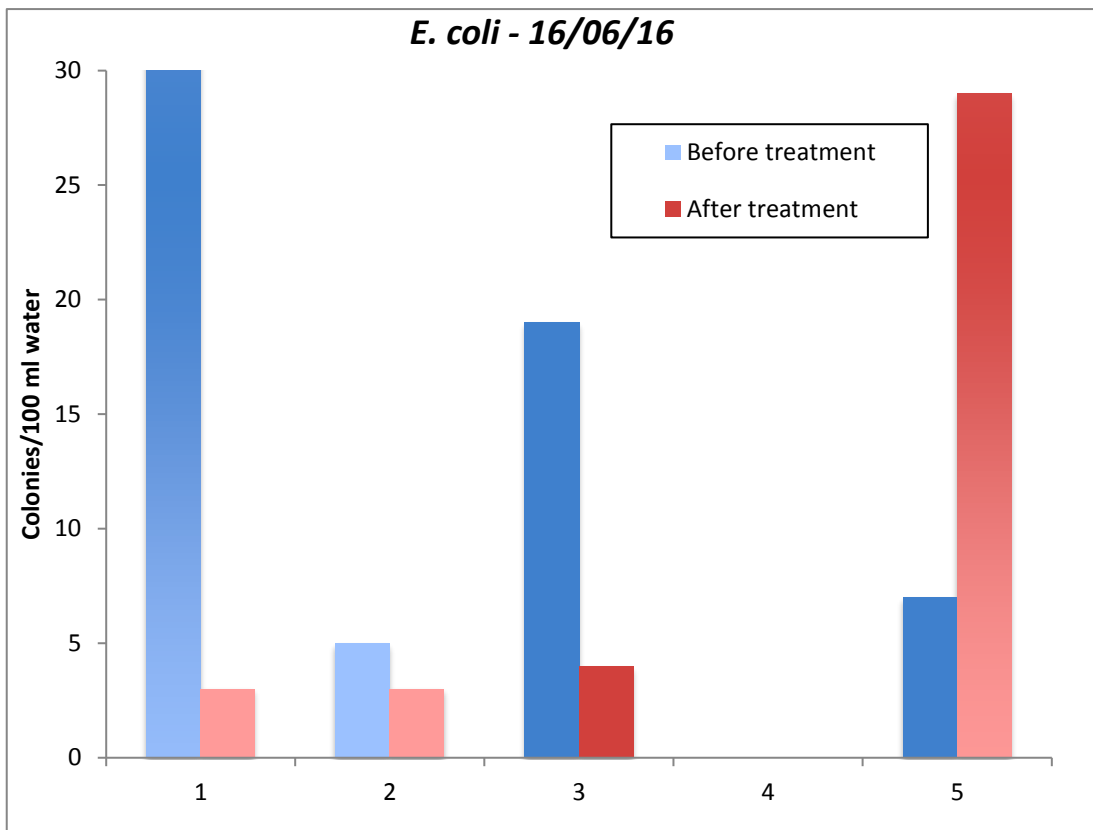
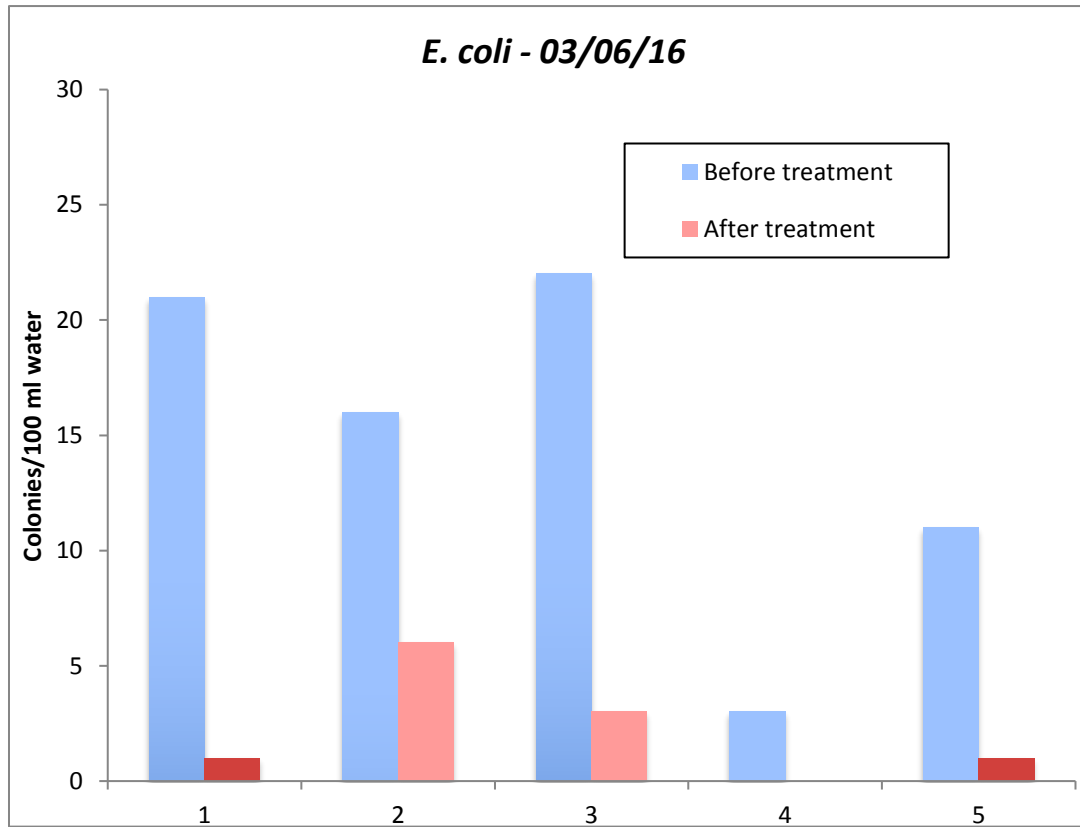


Figure 7: Microbiological tests (E. coli)

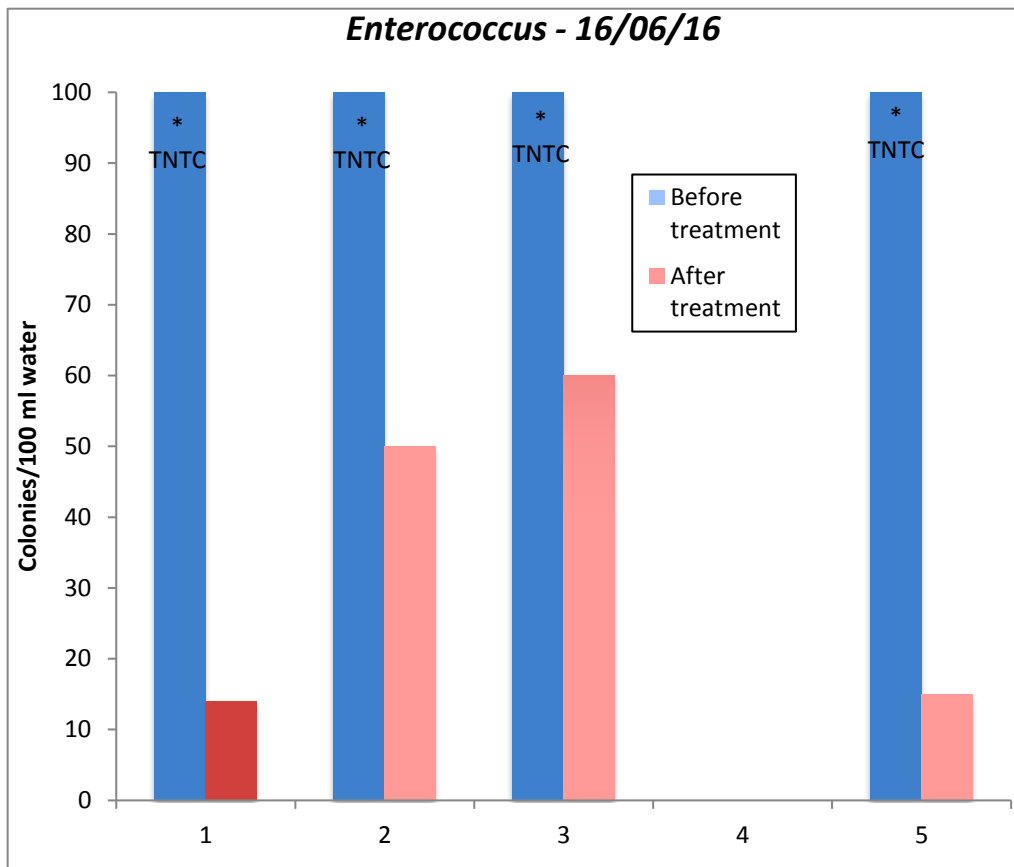
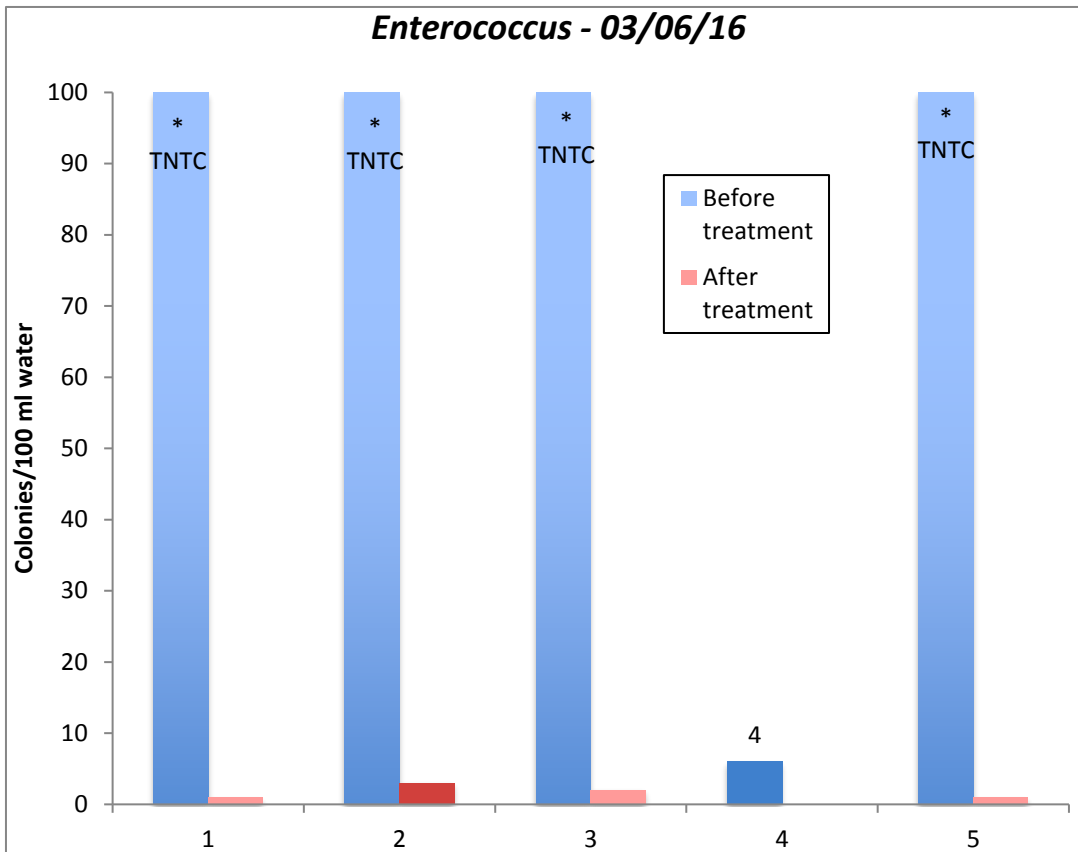


Figure 8: Microbiological tests (Enterococcus)

Water salinity is another factor that affects the rate of action of the dispersant on organic compounds. Nevertheless, in the EPA-based investigations of the MSL formula, there was no study done to determine the impact of the level of salinity on the functionality of the dispersant. However, in the different marine environments that the dispersant was applied to, such as coastal waters, beaches, ports and marinas, the MSL formula achieved the desired levels of reduction based on the resulting concentrations of the organic compounds. This means that salinity should not block the anti-pollution activity, however there is still a possibility that it could slow it down since different times of action were reported in each test. The waves and water currents are other important parameters that may affect the process of the MSL driven dispersion of organic compounds in marine environment. When there are waves and currents, it is easier for the dispersant to interact with the oil-water interface and reduce the surface tension. The waves and water currents also contribute to the dispersion by carrying and dispersing the tiny oil droplets to the maximum possible distance and allowing for an increased surface area for solar radiation to facilitate the process of evaporation. Microbes also play a major role in the breaking down of organic compounds through the natural biodegradation process. In marine environments that are rich in microbes, the process of degradation takes place more rapidly compared to environments where microbes have been destroyed by the chemical action of the pollutants. The MSL formula does not have any toxicity effects on the microbe population and thus their action and effectiveness should not be impacted. Finally, the concentration of organic compounds in the oil spill is the last factor that affects the rate of degradation following the treatment of the marine environment with the MSL. The higher the concentration of the organic pollutants, the longer it will take for the dispersant to carry out the optimum concentration reduction process. This explains why the rate of degradation is different for different types of hydrocarbon compounds such as the Arabian crude oil and the Total Petroleum Hydrocarbons (TPH).

Tests were carried out in several locations to determine the effectiveness of the MSL formula using different contaminant parameters: biological oxygen demand (BOD), chemical oxygen demand (COD), total petroleum hydrocarbons (TPH), and Fats oils and Grease (FOG). The results of these tests indicate that the MSL action was most effective on the TPH and FOG. The greatest changes after the treatment were observed in the COD and the BOD values, depending on the initial measurements. In conclusion, the use of MSL formula on all locations demonstrated its significant effectiveness on the parameters tested and confirmed the suitability of this environmentally friendly option as an antipollution agent in marine environments. The

application of MSL in different scenarios achieved comparable result, indicating that effectiveness is not dependent on location. This is an advantage to chemical dispersants that cannot be applied in places such as marinas, harbors and floating cage farming operations because of their toxic properties and non-biodegradability, which may cause secondary pollution to these environments.

An example of such a study was done at the Ayia Napa Port, where tests were carried out to assess the rate of reduction of different organic compounds under the MSL action. Among the organic compounds that were observed after varying durations of treatment included BOD, COD, FOG, and TPH as described above, and with TP and TKN as additional parameters. The concentration of these parameters was measured and recorded before the treatment was initiated. The concentration was then measured for all the parameters after treatment, with the duration of the treatment ranging from one to two weeks. It was noted that for all the parameters tested, there were significant reductions throughout the observation period. The remaining amounts were directly proportional to the initial amount for each parameter at the beginning of the treatment. The parameters that had comparatively higher concentrations at the beginning of the treatment also ended up with higher remaining concentrations at the end of the treatment period. This study was undertaken to assess the effectiveness of the MSL formula under different parameters and the results of the test confirmed its effectiveness under all parameters tested. Nevertheless, there are some instances where the weight of the parameters was observed to increase after a number of applications/treatments. This remains to be explained and further research needs to be conducted to find out the underlying cause/mechanism. For FOG and TPH, reduced levels were achieved after the second test and there was no further reduction. This could mean that the maximum possible reduction had already been achieved after the first two applications. The data that was obtained for the Ayia Napa Port Project is shown in Table 5.

Table 5: Results of Ayia Napa Port Project using the MSL formula (all dates 2015, all concentration values in mg/L)

	Before applicat (Aug 06)	After 1st applicat (Aug 10)	After 2nd applicat (Aug 27)	After 3rd applicat (Sep 14)	After 4th applicat (Oct 02)
BOD	80,00	<3,00	4,00	<3,00	<1,00
COD	483,00	14,00	7,00	<7,00	8,00
FOG	38,00	5,00	<1,60	<1,60	<1,60
TP	0,02	0,05	0,01	<0,04	<0,04
TKN	1,20	0,96	2,67	1,02	4,80
TPH	33,14	4,84	<0,17	<0,17	<0,17

The MSL formula is manufactured from plant extracts and has been known to exhibit several advantages over the more commonly used chemical dispersants. MSL is known to be rapidly and readily biodegradable and furthermore the product is non-toxic to marine environment. Unlike other chemical treatment methods, which are used for the cleaning up of marine environments from other pollutants of oil spillages, the MSL product is based on herbal formulas designed to enhance the effects that the clean up has on the environment and to promote the use of green technologies in addressing the environmental concern. It is an efficient solution that does not cause secondary pollution nor does it have any effect on the aquatic ecosystem. The application of the MSL formula is also cost-effective compared with conventional chemical dispersants. The use of green technologies to curb environment pollution and to perform cleanup of the polluted environment is of growing interest and many researchers and scientists are continually discovering and patenting solutions that are claimed to be environmentally friendly. However, for any green oil dispersant or any other cleanup solution to be recommended for commercial use, it needs to meet the EPA set conditions for the dispersion efficiency and biodegradation rate (Theodorou, 2017).

The MSL formula is the green herder technology that was the focus of this study. This is an efficient, eco-friendly, innovative product that is based on natural ingredients (plant extracts). MSL does not pollute or disturb the marine environment, is non-toxic and has the ability to restore the delicate balance of marine ecosystems. The efficiency of the MSL formula, assessed on Arabian crude oil according to the EPA recommendations for dispersants, was found to be at 86.36%. Maximum degradation rate was found to be 90.48% after 96 hours when tested, again on Arabian crude oil. The MSL formula has been investigated and found to be suitable for different marine environments, such as coastlines and beaches, harbors and marinas, and floating cage-farming operations.

Most dispersants used in sea waters do not exhibit significant levels of toxicity and are similar to those of common household items such as shampoos and liquid dish wash solutions (Word et al., 2015). However, these dispersants are chemicals and when added to an area that is already negatively impacted by an oil spill, the result is an increase in the levels of pollution in the affected area. Furthermore, when an oil slick is dispersed, it further mixes toxic substances into the water thereby proving hazardous to living organisms (Prince, 2015). The MSL product indicated considerably lower levels of toxicity in similar situations.

Phytoremediation is a promising technology since it is cost-effective, has aesthetic advantages, is biodegradable, and has long-term applicability (Das & Chandran, 2011). Nevertheless, this technology also has some challenges wherein there is little data regarding the removal rates and efficiencies of the contaminants that are directly attributable to the plants under field conditions. Nevertheless, phytoremediation does not involve the use of plant extracts as an anti-pollution solution since this method relies on the use of living plants. In this regard the MSL formula has also proven to be an effective and eco-friendly anti-polluting agent.

V. CONCLUSIONS

A comprehensive discussion of plant extracts as an antipollution solution in water column is discussed in this paper. The mechanism through which these extracts achieve their antipollution effects and whether they meet the EPA Regulatory Protocol guidelines for an acceptable dispersant has also been investigated. Different methods used for the cleaning up of the marine environment were identified wherein the use of herding process is identified to facilitate the in-situ burning. The second method that was discussed is dispersion with the use of dispersive agents. The third method, although not practical in all situations, is the selective absorption of the polluting organic compounds through the use of materials that can selectively attract the organic compounds while at the same time repelling the water.

Traditionally, chemical approaches have been employed for these latter two processes. However, it has been shown that chemical approaches result in secondary pollution of the marine environment. In order to address this issue, green alternatives have been identified that have distinct advantages over chemical herders. One such green herder is the MSL formula, which is an eco-friendly solution based on natural ingredients (plant extracts). It has no adverse impact such as toxicity and secondary pollutant effects. Tests were carried in on different locations such as the Ayia Napa Port, Nissi Beach, and Larnaca Marina to assess the effectiveness and economic viability of treating with the MSL product. These tests demonstrated that the MSL formula is effective and suitable for different areas such as coastlines, beaches, and marinas. The present study investigated the action of MSL on Arabian crude oil. Through the experiments that were performed, it was assessed that the efficiency was 86.36% and a degradation rate of 90.48% after 96 hours for the same specimen. This was above the EPA recommended standards for a viable oil dispersant. The results showed that plant extracts have the potential to act as eco-friendly, biodegradable, non-toxic, and cost-effective alternatives for anti-polluting agents in marine environments.

In the study undertaken to assess the effectiveness of the MSL formula, the results confirmed the superior characteristics of the product under all parameters tested. Further studies are required to explain the abnormal behavior where an increase in concentration of some parameters was observed when the MSL formula is used to cleanup a polluted marine environment. Further research is also needed to explain the possible minimum concentration that some organic substances attain after treatment with the MSL formula and below which no further reduction can be achieved.

Following the conclusion of this research study, it is clear that further studies are recommended regarding the use of MSL as a plant extract formulation suitable for mitigating the harmful effects of organic pollutants in marine environments. For example, the effect of seawater salinity on the effectiveness of the MSL formula has not yet been identified. According to the literature, it has been shown that salinity has an impact on the action of chemical dispersants when used on hydrocarbons. The effects of salinity on the MSL action needs to be investigated so that the optimum conditions for the use of the MSL formula can be determined in order to minimize the environmental and financial damages from oil spill incidents.

Sunlight plays both a negative and positive role in the process of degradation. Continued exposure of the organic compound and dispersant mixture to direct sunlight results in the formation of sludge. Sludge cannot degrade easily and slows down the natural

degradation since microbes cannot act on the sludge as efficiently as they can on the tiny droplets of dispersed oil spills. The positive role that sunlight plays on the degradation process is the consequent dispersal after the oil has been broken down through the process of dispersion. Therefore, further tests need to be conducted to determine whether sunlight could potentially have the same negative role on the oil spills following treatment with MSL. This will help set the optimum conditions in order to achieve the maximum possible efficiency of the MSL formula.

VI. ACKNOWLEDGEMENTS

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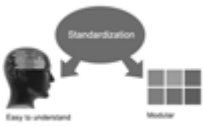


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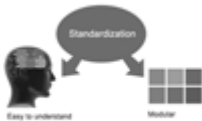
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TECHNIQUES FOR WRITING A GOOD QUALITY RESEARCH PAPER:

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30. Think and then print: When you will go to print your paper, notice that tables are not be split, headings are not detached from their descriptions, and page sequence is maintained.

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<i>References</i>	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring



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