Influence of dispersants on BTEX contamination in a deep oil spill

Influencia de los dispersantes en la contaminación por BTEX en un derrame profundo de hidrocarburos

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Abstract

Information on catastrophic events such as the one that occurred in the "Deepwater Horizon" Platform in the Gulf of Mexico in 2010, is used to analyze the influence of chemical dispersants in the contamination by benzene, toluene, ethylbenzene, and xylene (BTEX) in a hydrocarbons deep spill. The research analyzed the variability of BTEX concentration fields in a volume of oceanic water in relation to the use of chemical dispersants in a deep spill, keeping constant the oceanographic conditions of the affected area, such as, thermohaline stratification, the currents fields of and the characteristics of the spilled fluid. The results of this research showed that the use of chemical dispersants in a spill at high depths increases the contamination by BTEX, that is not detectable by remote sensing and visual observations.

KEYWORDS: hydrodynamic model; deep spill; BTEX; eulerian approach.

Resumen

La información de eventos catastróficos como el ocurrido en la Plataforma "Horizon Deepwater" en el Golfo de México en el año 2010, se utiliza para analizar la influencia de los dispersantes químicos en la contaminación por benceno, tolueno, etilbenceno, y xileno (BTEX) en un derrame profundo de hidrocarburos. La investigación analizó la variabilidad de los campos de concentración de BTEX en un volumen del agua oceánica con relación al uso de dispersantes químicos en un derrame profundo, manteniendo constantes las condiciones oceanográficas de la zona afectada, tales como, la estratificación termohalina, los campos de corrientes y así mismo las características del fluido derramado. Los resultados de la investigación demostraron que el uso de dispersantes químicos en un derrame en altas profundidades, incrementa la contaminación por BTEX, no detectables por los sensores remotos y observaciones visuales.

PALABRAS CLAVES: *modelo hidrodinámico; derrame profundo; BTEX; Aproximación euleriana.*

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Introduction

Millions of barrels of oil emerged from the seabed of the Gulf of Mexico as of April 20, 2010, after the sinking of the Deepwater Horizon Platform (DWH, Macondo well), 1.5 km deep. (Reddy *et al.,* 2012).

Numerical models have been developed and studied to understand the physical behavior and transport of hydrocarbons in a deep spill in the marine environment (Yapa *et al.,* 2012; Bandara & Yapa, 2011; Johansen, 2000; Lee & Cheung, 1990; Spaulding *et al.,* 2000, Udita & Poojitha, 2011, Yapa & Chen, 2004, Zheng & Yapa, 2001).

In any spill, the benzene, toluene, ethyl-benzene, and xylene compounds (BTEX) are of particular interest (Reddy *et al.,* 2012), especially due to their degree of toxicity. In vitro studies suggest that benzene could cause chromosomal breaks and interfere with chromosome segregation; Toluene is neurotoxic and teratogenic; chronic exposure to xylene is associated with harmful effects on the nervous system, liver and kidneys (Christofoletti *et al.,* 2011).

Marine biology studies have shown traces of BTEX inside the carcasses of marine corpses after the oil spill of the Exxon Valdez ship in Prince William Sound, Alaska in 1989 (Ballachey & Kloecker, 1997).

Models developed in physical and chemical oceanography have exposed that the aromatic compounds are solubilized in the water column at high depths and are part of the contamination caused by the most toxic hydrocarbon fractions, not detectable by remote sensing and visual observations (Rodriguez & Lonin, 2017).

To minimize the impacts of oil spills at sea, oil companies often use chemical means, such as dispersants. A dispersant is a mixture of solvents, additives and surfactants. These reduce the surface tension by a factor of 20 or more, decreasing the average size of the drops formed due to the turbulent shearing of the fluid (Li & Garret, 1998). The dispersants that are applied directly to the head of the well, modify the physical and chemical properties of the oil that springs from a deep leak, dividing it into tiny drops of only 10 microns in diameter (Schmidt, 2011). The decision to use dispersants always omits environmental counterparts. Undispersed oil floats on water, affecting birds and marine mammals and contaminating coastal resources. However, the dispersed oil and its components are transported inside the water column, impacting the first level of the marine food chain (Schmidt, 2011).

It is estimated that around 7 million liters of dispersant were used in the DWH incident, so it is also inferred that 3 million liters correspond to underwater addition near the discharge. In principle, with a flow of 45 liters / minute, later reduced to 26 liters / minute. The Environmental Protection Agency (EPA) imposed the maximum underwater use of dispersants of 39.36 liters/minute (Lehr *et al.,* 2010).

Products used as dispersants in the DWH spill, contain: 2-butoxyethanol (3-BE), sulfonic organic acid salts as a surfactant, and propylene glycol as a stabilizer (Schmidt, 2011). The National Technical Committee of the National Contingency Plan PNC (1999) is responsible in Colombia for the authorization of dispersants. (Miranda, *et al.,* 2008).

In the present investigation, a numerical modeling of the spill in DWH was carried out under the oceanographic conditions registered at the time of the accident, and the importance of the behavior of the soluble part of hydrocarbons in conditions of dispersant use was demonstrated.

Methodology

In the present investigation the hydrodynamic model ECOMSED *[Three-dimensional Hydrodynamic and Sediment Transport Model,* (HydroQual, 2007)] was used for the simulation of the Eulerian fields of BTEX, the source for which was the Lagrangian plume of the deep spill with and without the application of chemical dispersants.

In other words, the investigation analyzed how the concentration of BTEX in an oceanic water volume changes in relation to the use of chemical dispersants in a deep spill, keeping constant the conditions of the affected area, such as thermohaline stratification, fields of currents, and sea level topography, and likewise the characteristics of the spilled fluid.

To simulate the behavior of BTEX solubilized in a deep hydrocarbon spill, it was necessary to know the Lagrangian behavior of the trajectory of the plume in 3D for oil spilled with and without the use of dispersants.

In the Lagrangian model, each particle of the hydrocarbon plume was specified in a spherical shape, characterized by its location in three dimensions.

In general, in a deep spill of hydrocarbons, the typical sizes of the drops generally vary from 1 to 10 mm. A methodology for calculating oil droplet size distributions has recently emerged. Studies have shown a comparison between the computational and experimental distribution of droplet size (Yapa *et al.,* 2012).

According to Yapa *et al.,* (2012) the typical sizes of the drops based on experimental methods have a predominant distribution in diameters that oscillate between 2, 3 and 4 mm, however, this distribution is different in the presence of chemical dispersants; in this situation a distribution by diameters between 600, 700 and 800 µm prevails (Yapa *et al.,* 2012).

At the spatio-temporal scale where the DWH spill occurred in June 2010, the representation of the transport processes in the ocean had to be adjusted, registering a geographical position of the platform of 28 ° 12 'N, 88 ° 48' W (Conabio, 2010).

The domain of the model (35 x 35 km) was centered at the site of the DWH spill. The studies developed by Reddy, *et al.,* (2012) on the behavior of the soluble part were taken into account; according to this work, the dilution is negligible in distances greater than 27 km from the origin (Reddy *et al.,* 2012; Zhengzhen *et al.,* 2013).

It was necessary to adapt the thermohaline information available in the simulation of the model by means of a previous cold start to achieve a resolution of 500 meters (Locarnini, *et al.,* 2015). Information on temperature and salinity profiles for the construction of the thermohaline fields for different dates was found at the following site: https://www.nodc.noaa.gov/deepwaterhorizon/. The Table 1 shows the characteristics of hydrocarbons introduced into the model.

Table 1. Parameters used in the simulation.

Oil discharge rate - m^3/s	0.0184
Oil density - kg/m^3	920
Diameters of oil drops without the use of dispersants – m	0.002 / 0.003 / 0.004
Diameters of oil drops with use of dispersants – m	0.0008 / 0.0007 / 0.006

The Figure 1 shows the fixed and modeled fields of salinity and temperature at 500 meters depth, respectively.

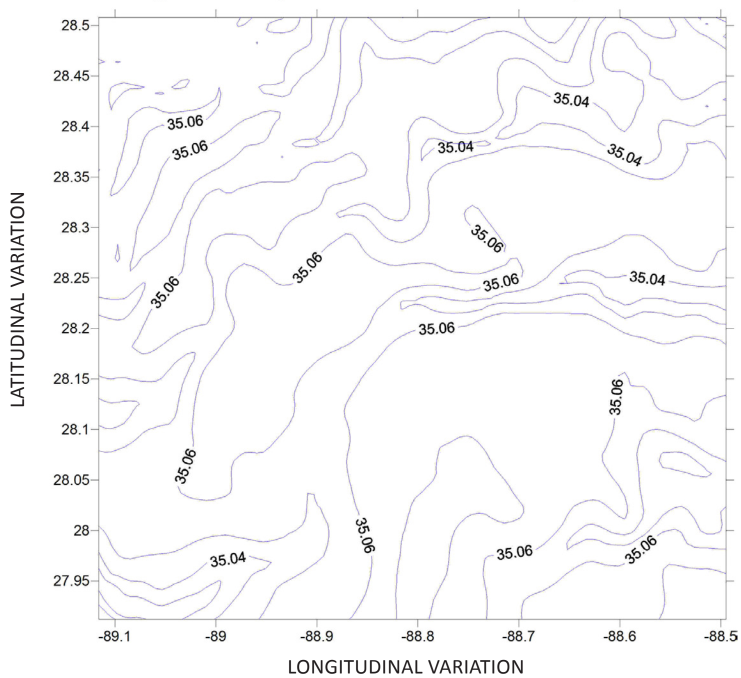

Figure 1A. Salinity field at 500 meters depth.

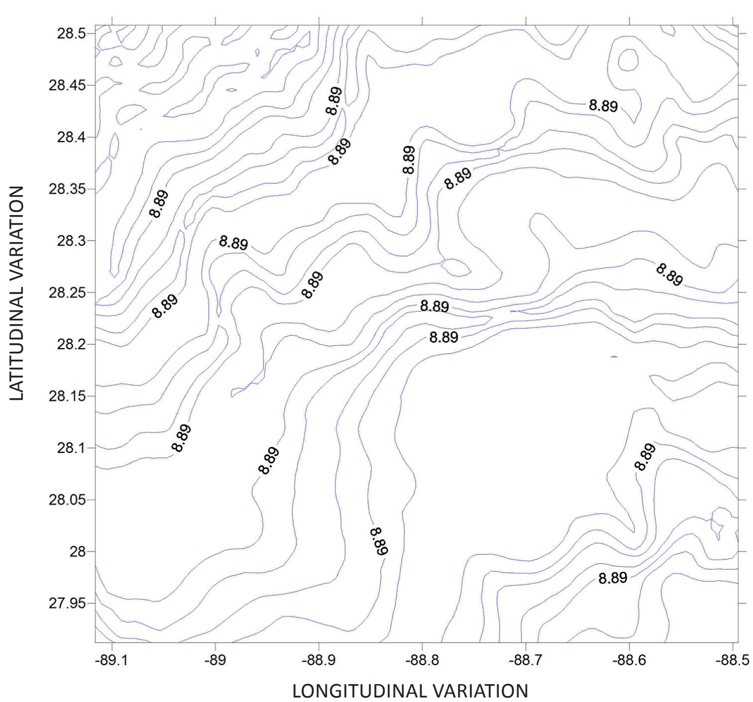

Figure 1B. Temperature field (ºC) at 500 meters depth.

The Figure 2 shows the fields of currents, the result of running the ECOMSED hydrodynamic model on June 12, 2010.

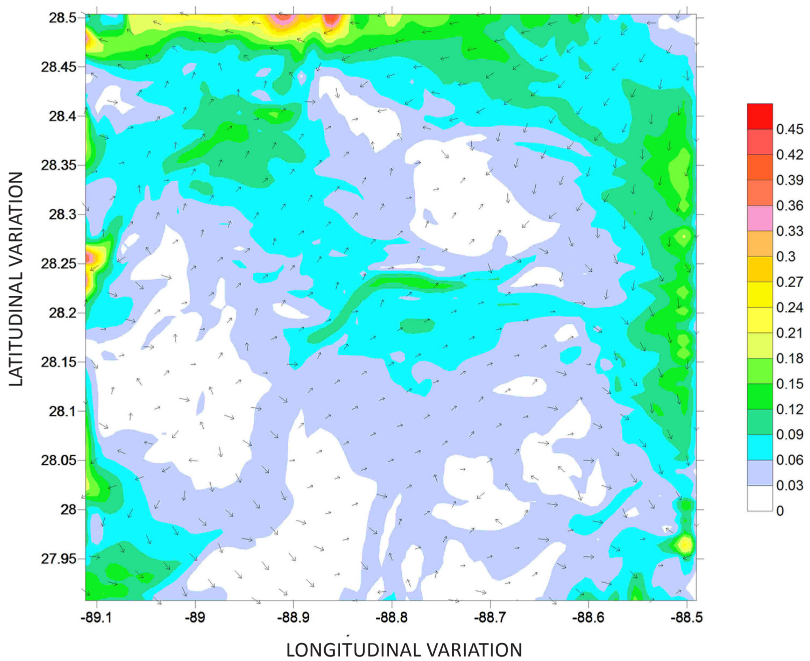

Figure 2A. Currents at 500 meters depth.

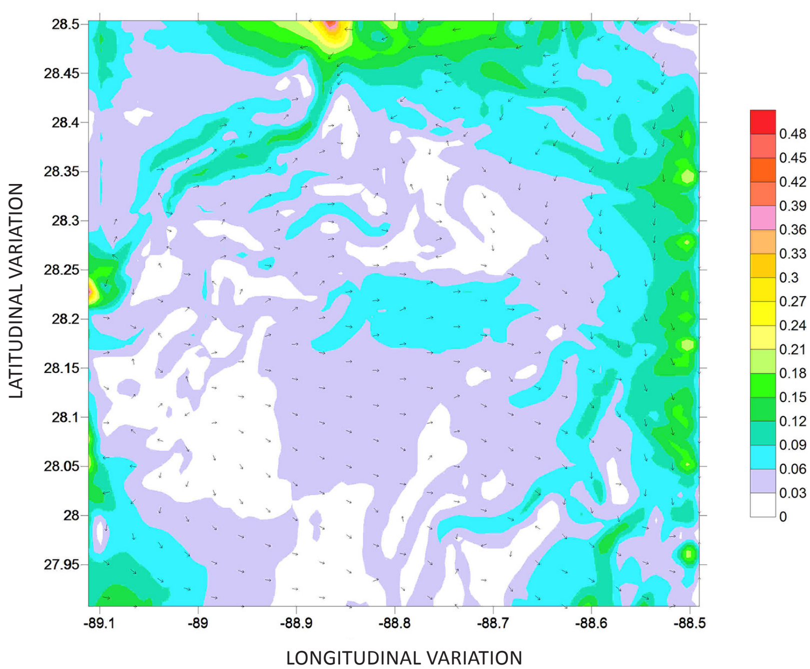

Figure 2B. Currents at 1000 meters depth.

The behavior of the plume of an oil spill is influenced by various physical and chemical processes, among which is the formation of methane hydrates. However, in the model described in this research, the dynamics of the plume does not include the physical-chemical processes associated with the formation and dissolution of gas hydrates (Chen & Yapa, 2004).

The volumes of the cells in the calculation grid for the construction of the Eulerian model of solubilized BTEX were defined as fixed control volumes around each drop of the Lagrangian plume, so it is important to indicate that this operates for both cases, with and without chemical dispersants.

For both models (with and without dispersants) the duration and the mass discharge of the spill were defined to be similar. Other parameters were calculated as variables in the model since they are dependent on the drops diameter. For example, the mass transfer coefficient should be calculated for each condition to be analyzed (Branan, 2000).

The rate of change in the mass of BTEX contained in the drops with and without dispersants, due to the dissolution in the water column, was expressed by the following equation (Zheng & Yapa, 2001):

$$\frac{dn}{dt} = -KA(S - C_a) \qquad \textbf{(1)}$$

Here, *t* es time; *n* is the number of moles of solubilized component; *K* is the mass transfer coefficient for BTEX (m / s); A is the total surface area of each of the drops in the liquid phase (m^2); *S* is the solubility of BTEX (mol / m^3) and C_a is the existing concentration of BTEX dissolved in the environment (mol / m^3). Then, it was assumed that C_a en *(1)* es negligible ($C_a << S$).

For each condition of the deep oil spill, with and without the use of dispersants, the concept of the effective internal coefficient was used, just as it is applied for the transfer of heat in solid spheres (McCabe *et al.,* 2007):

$$K = \frac{10 D_V}{D_p} \qquad \textbf{(2)}$$

Herein, D_v is the diffusion inside the drop (m^2 / s); D_p is the diameter of the drop (m).

The transport of substances is affected by factors such as currents, turbulent diffusion processes and even the phase change of pollutants (solubility). The respective transport equation is described below:

$$\frac{\partial C}{\partial t} + \frac{\partial CU}{\partial x} + \frac{\partial CV}{\partial y} + \frac{\partial CW}{\partial z} = \frac{\partial}{\partial z}\left(K_H \frac{\partial C}{\partial z} \right) + F_c + Q \qquad \textbf{(3)}$$

In (3), *C* is the concentration of the pollutant, transported at time t and in space (x, y, z) for the respective components *U, V* and *W* of currents; *Q* is the internal source due to the dilution of BTEX components (kg / m^3 / s), and *Fc* represents horizontal diffusion.

In the given case, *Q* is the rate of BTEX accumulation from the Lagrangian plume and is defined by equations (1) and (2).

The conditions in the open contours of the model were defined as *C = 0*, under the consideration that they are sufficiently distant from the source of origin. The initial condition was defined as *C (t = 0) = 0 (t = 0)* corresponds to the beginning of the deep spill). For the representation of BTEX behavior, only benzene was considered. On the surface of the sea and on the ocean floor, the benzene flow is assumed to be zero. (If for the seabed this condition is fully applicable, the zero flow on the sea surface is assumed under a certain approximation due to the possibility of evaporation of the substance). The necessary parameters for (1) and (2) are defined in Table 2.

Table 2. Parameters of the fluids in the simulations (Vp represents the volume of a particle / drop, NTD is the total number of drops in the simulation).

Properties of the fluid without the use of dispersants (for three sizes of drops)				
Dp (m)	**Dv (m2/s)**	**K (m/s)**	**Vp (m3)**	**NTD**
0.002	1.49	0.00000745	4.1888E-09	4.12116E+13
0.003	1.49	4.96667E-06	1.41372E-08	1.22108E+13
0.004	1.49	0.000003725	3.35104E-08	5.15145E+12
Properties of the fluid with the use of dispersants (for three sizes of drops)				
Dp (m)	**Dv (m2/s)**	**K (m/s)**	**Vp (m3)**	**NTD**
0.0008	1.49	0.000018625	2.68083E-10	6.43931E+14
0.0007	1.49	2.12857E-05	1.79594E-10	9.61203E+14
0.0006	1.49	2.48333E-05	1.13098E-10	1.52635E+15

The final validation of the obtained BTEX concentration fields was not carried out due to the lack of detailed in-situ observations of the diluted substances. However, the concentrations of BTEX calculated with the use of dispersants, agree in the order of magnitude with data given in technical reports (Reddy *et al.,* 2012).

Results and Discussion

The use of chemical dispersants in deep oil spills impacts the behavior of the solubilized phase of BTEX in the marine environment. The application of the Eulerian model made it possible to quantify the variation of BTEX diluted in the water column when using chemical dispersants in a deep oil spill.

The Figures 3A-3F represent the variations of BTEX concentration within the study domain for June 12, 2010 at 1,200, 750 and 250 meters depth, with and without the use of chemical dispersants.

The distribution of BTEX concentration had spatial variation in three dimensions. Since the origin of the oil spill is in the center of the domain, a significant variation of the benzene field at different depths is observed when the oil spill is influenced by the use of chemical dispersants.

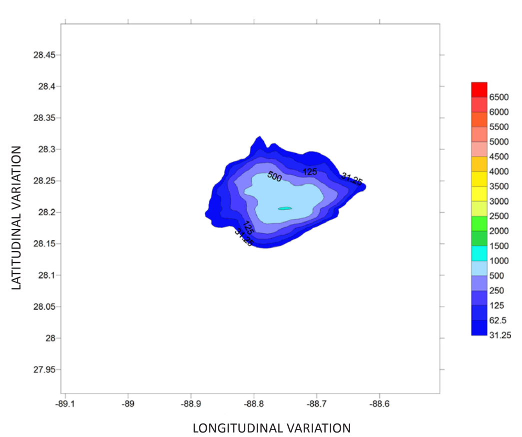

Figure 3A. BTEX field (ppb) at 1200 m, with dispersants

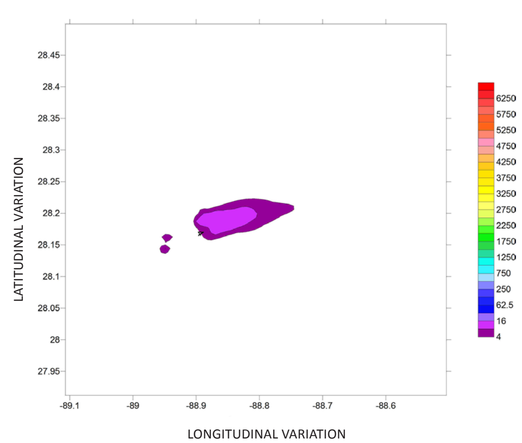

Figure 3B. BTEX field (ppb) at 1200 m, without dispersants.

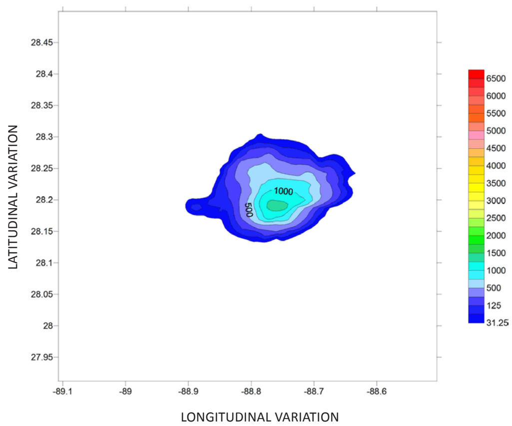

Figure 3C. BTEX field (ppb) at 750 m, with dispersants.

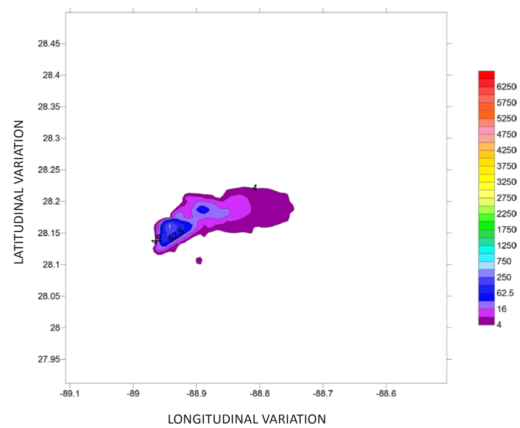

Figure 3D. BTEX field (ppb) at 750 m, without dispersants.

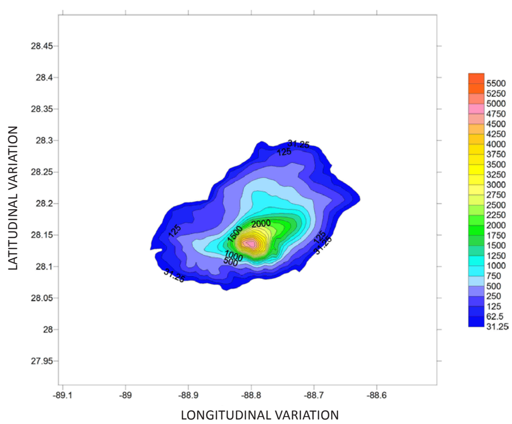

Figure 3E. BTEX field (ppb) at 100 m, with dispersants.

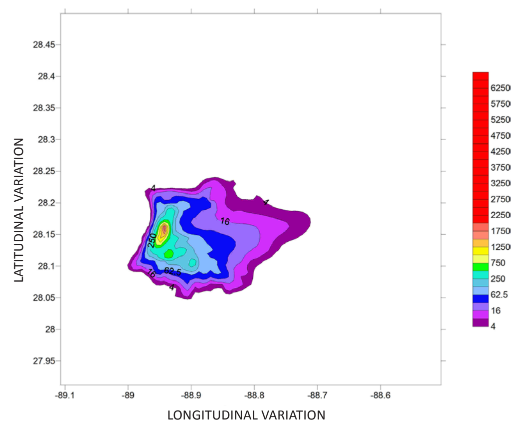

Figure 3F. BTEX field (ppb) at 100 m, without dispersa.

The BTEX field at 1200 m depth shows a concentration change of 16 ppb without dispersants to 500 ppb with them. For the BTEX field at 750 m depth, a concentration change of 62 to 1500 ppb is observed without and with chemical dispersants, respectively. At 100 m depth, this variation is from 250 to 2000 ppb for the same cases.

According to the mass transfer rat and the horizontal mixing processes, the concentration field has a concentric and ring behavior, in all scenarios, decreasing towards the peripheral part of the spill.

The mentioned results showed an increase in the concentration of BTEX between 8 and 30 times, approximately, in the case of the use of dispersants in the model. Let's do some simple estimates. As noted in the methodology, in average, the diameter of a drop in a blowout is $D_0 = 3\ mm$, while the use of dispersants decreases this value to $D_1 = 0.7\ mm$. The latter implies that the reason for the volumes of drops with and without dispersants is given by $(D_1/D_0)^3 << 1$, where the increase in the number of drops N must be characterized as $(D_1/D_0)^3 = 1/N$. With the values taken from the droplet diameters, this proportion indicates an increase in the number of droplets $N = 78.7$ times greater than in a spill without dispersants.

If with this estimate the increase in the contact area between the drops and the water is sought, then in the case of the use of dispersants, the increase is $(D_1/D_0)^2 N = 4.3$ times, approximately.

Therefore, the decrease in the size of the drops and the increase in the contact surface with water (increase in the number of drops), increases the possibility of solubility of the BTEX compounds. This result shows that the mass transfer coefficient *K* in formulae (1) is inversely proportional to the diameter of the drop (formulae 2). The *K* value increases 4.3 times in the example. The numerical model presents the same order of magnitude of the resulting concentration, and is effectively sensitive to the distribution of the drops by size.

Conclusions

It is important to note that it was possible to demonstrate the impact of dispersants on BTEX contamination in a deep oil spill. The application of the Eulerian model made it possible to quantify the variation of BTEX diluted in the water column both with and without the use of chemical dispersants.

The Eulerian model for these conditions, with and without chemical dispersants, took into account measurable variables such as thermohaline stratification, initial hydrocarbon composition in the spill and other physical characteristics of the environment to simulate the behavior of the plume.

The hydrodynamic model ECOMSED (HydroQual, 2007) was adapted to the simulation of the behavior of the soluble components in the example case of the 2010 deep oil spill in the Macondo well. The modeling showed that the use of dispersants increases the amount of the soluble fraction of hydrocarbons.

The change in the concentration of the BTEX components solubilized in the water column demonstrated that it may not be negligible. It is recommended to include in the environmental assessments, the application of this type of tools for licenses, prior to the activities of exploitation of natural resources offshore given the degree of toxicity of these compounds for living organisms.

This knowledge is important for the planning of future policies related to the use of dispersants in Colombia, headed by the National Technical Committee of the National Contingency Plan (PNC).

The results of this study illustrated that it is indispensable to make academic and technological efforts in order to find alternatives to the use of dispersants in a deep spill.

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