The 2014 International Conference on Marine and Freshwater Environments

iMFE 2014

Joint Conferences:
The 2014 Annual Conference of the International Society for Environmental Information Sciences (ISEIS)
The 2014 Atlantic Symposium of the Canadian Association on Water Quality (CAWQ)
The 2014 Annual General Meeting and 30th Anniversary Celebration of the Canadian Society for Civil Engineering Newfoundland and Labrador Section (CSCE-NL)
The 2nd International Conference of Coastal Biotechnology (ICCB) of the Chinese Society of Marine Biotechnology and Chinese Academy of Sciences (CAS)

Behavior of Corexit dispersants in the Gulf of Mexico after the Deepwater Horizon oil spill

Qinhong Cai[1], Baiyu Zhang[1,*] Bing Chen[1], Pu Li[1], Xing Song[1] and Zhiwen Zhu[1]

[1]*The Northern Region Persistent Organic Pollution Control (NRPOP) Laboratory, Faculty of Engineering and Applied Science, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X5*

[*]*Corresponding Author's Email address; bzhang@mun.ca*

Abstract

Offshore Oil spills are of tremendous concern due to its enormous harm to economic and ecological systems. Corexit dispersants are used as an important combating agent for oil spills as they can dilute oil downward to water column and promote its biodegradation. They were extensively used during the Deepwater Horizon oil spill and dispersed 16% of the spilled oil. The aims of this paper was to illustrate the transport and fate of the key ingredient of Corexit dispersants, dioctylsulfosuccinate, sodium salt (DOSS), in the Gulf of Mexico after the Deepwater Horizon oil spill. Relevant data were collected from literature and governmental databases. Subsequently, the distribution of DOSS was correlated with distributions of the flow of diverse hydrocarbons. The results indicated that DOSS had highest distribution correlation coefficients with gases and BTEX. The smaller molecular gases and aromatic compounds have higher distribution correlation coefficients while larger molecular alkanes have higher distribution correlation coefficients. The obtained correlation would provide useful information on the fate and behaviour of Corexit dispersants.

Keywords: Corexit dispersants, correlation, dioctylsulfosuccinate, sodium salt (DOSS), hydrocarbon flow

Introduction

The catastrophic Deepwater Horizon oil spill occurred on April 20, 2010 threatened over $5.5 billion fishing and tourism industrial economic entities and more than 200,000 employment opportunities (Hagerty and Ramseur, 2010). Millions of seabirds and billions of fish eggs (Corn and Copeland, 2010) were killed and a dramatic population decline and shift of microorganisms, phytoplankton and other flora were observed (Widger et al., 2011). Reddy et al. (2012) collected samples directly from the Macondo well on June 21, 2010 and found that the released oil and gas had the composition showed in **Table 1**. The top three released gas components were methane, ethane and propane while the top three released oil components were alkanes, alkybenzenes and polycyclic aromatic hydrocarbons (PAHs).

Table 1. Composition of the released oil and gas from Macondo well on June 21, 2010 (Reddy et al., 2012)

Gas	Content, %	Oil	Content, %
Methane	82.5	Saturated alkanes	0.57
Ethane	8.3	Alkylbenzenes and indenes	0.09

Propane	5.3	Polycyclic aromatic hydrocarbons	0.039
Butane	2.87	Biomarkers	0.016
Pentane	1.04	Others	0.18

Within the first week of the Deepwater Horizon oil spill, the use of dispersants was approved by the first-acting federal on-scene-coordinators (OSCs) in order to fight this spill as far away from the coastline as possible. In total, 1.07 million gallons of Corexit dispersants (Corexit 9500 and Corexit 9527) were applied on the surface, while 771,000 gallons were applied to the subsea discharge point (National Commission Final Report, 2011). Dispersants consist of surfactants and solvents. Solvents help deliver the surfactants into the oil/water interface where surfactants change the interfacial properties and beak down oil slicks into small droplets. They were used to reduce the impact of oil on the shorelines, birds and mammals living on the water surface as well as to promote the biodegradation of oil (Board of Ocean Studies, 2005).

The USEPA has provided benchmarks based on available ecological data to aid in the assessment of potential risk associated with dispersant chemicals. Among these dispersant chemicals, the surfactant, Dioctylsulfosuccinate, sodlium salt (DOSS), has the lowest benchmark value and is of the highest toxicity.

DOSS was used as the tracer of the polar components of Corexit 9527 and 9500A in seawater (Gray et al., 2014; Kujawinski et al., 2011). Kujawinski et al. (2011) also measured in-situ methane concentration when they took their samples for DOSS analysis and found out nearly 1:1 distribution correlation between DOSS and methane. Valentine et al. (2010) investigated dissolved hydrocarbon gases at depth from June 11-21, 2010. They found methane was not substantially biodegraded but instead was transported conservatively with deep ocean currents. Kujawinski et al. (2011) thus speculated that DOSS behaved similarly as methane and this speculation was validate with experimental data. This study demonstrated the finding distribution correlation between DOSS and other well studied hydrocarbon compounds could be of great significance in terms of understanding the behavior of dispersants in the ocean columns. However, no one attempted to correlate DOSS with other hydrocarbons released during the blowout that interacted with DOSS. As robust databases concerning the Deepwater Horizon oil spill were available, the analysis could be straightforward yet meaningful in terms of providing helpful information on the fate and behavior of Corexit dispersants.

In the present study, we used database of Deepwater Horizon oil spill to evaluate the distribution correlation between DOSS and hydrocarbon flow. In the meantime, the risk (hazard quotient) of DOSS in terms of fish intake by residents in the vicinity of the affected areas was assessed with Monte Carlo simulation and the corresponding uncertainty was also evaluated.

Materials and Methods

Data Acquisition

The analytes used in this study and their sources were listed in **Table 3**. All these datasets consisted of latitude (N^o), longitude (E^o), Elevation (m) and concentration of the analytes. For

DOSS distribution, data from Kujawinski's group and Gray's group were used (Gray et al., 2014; Kujawinski et al., 2011). The data between May 25 and June 21 from both groups were combined together. For gases, data from the study of Valentine et al. (2010) were used. As these data only obtained between June 11 and June 21, the distribution correlations were established between data within this timeframe. For BTEX, 2-3 ring aromatic compounds and 4 ring aromatic compounds, the data were obtained from the database prepared by Centre for Offshore Oil Gas and Environmental Research (COOGER), Department of Fisheries and Oceans (DFO), Canada. The datasets were downloaded from the National Oceanographic Data Center (NODC, 2014). The data between May 25 and June 21 were used. For total aromatic compounds, total alkanes and n-alkane of different sizes, the data were the combined results from database of both COOGER, DFO, Canada and NOAA's Query Manager data management system which primarily collected data provided by USEPA. The datasets were also downloaded from the National Oceanographic Data Center (NODC, 2014). The data between May 25 and June 21 were used.

Table 3. Parameters used in this study and the corresponding sources

Parameters	Sources
DOSS (µg/L)	Kujiawinski et al., 2011 and Gary et al., 2014
Methane (nM)	Valentine et al., 2010
Propane (nM)	Valentine et al., 2010
Butane (nM)	Valentine et al., 2010
BTEX (µg/L)	Centre for Offshore Oil Gas and Environmental Research (COOGER), Department of Fisheries and Oceans (DFO) Canada
2-3 ring aromatic compounds	COOGER, DFO, Canada
4 ring aromatic compounds	COOGER, DFO, Canada
Total aromatic compounds	COOGER, DFO, Canada and NOAA's Query Manager data management system
10 C alkane (µg/L)	COOGER, DFO, Canada and NOAA's Query Manager data management system
14 C alkanes (µg/L)	COOGER, DFO, Canada and NOAA's Query Manager data management system
20 C alkanes (µg/L)	COOGER, DFO, Canada and NOAA's Query Manager data management system
Total alkanes (µg/L)	COOGER, DFO, Canada and NOAA's Query Manager data management system

Data Analysis

The plots of the distributions of DOSS and other 11 analytes were visualized with MATLAB (the MathWorks, Inc, Natick, USA). As the special coordination of the 11 analytes were not necessarily coincident. The data used for the distribution correlation analysis were interpolated results from the raw data based on the “nearest” interpolation using MATLAB. The 11 analytes were interpolated to the spatial coordination data of DOSS. The plot of distribution correlation and corresponding coefficients (r^2) were obtained with Excel. The correlation coefficients (Pearson's r, Kendall's tau and Spearman's ρ) and the corresponding *p* values were calculated with SPSS Statistics version 19 (IBM, Armonk, USA).

Results and Discussion

Distribution of DOSS and hydrocarbons

The distribution of DOSS based was visualized in **Figure 1**. Between May 25 and June 21, Corexit dispersants were continuously added both at the surface and well head (The White House Blog, 2010). The distribution of DOSS was found to concentrate at both well head and the surface of ocean that with the same Latitude and longitude of the well head which were corresponding to the location of the continuous DOSS addition.

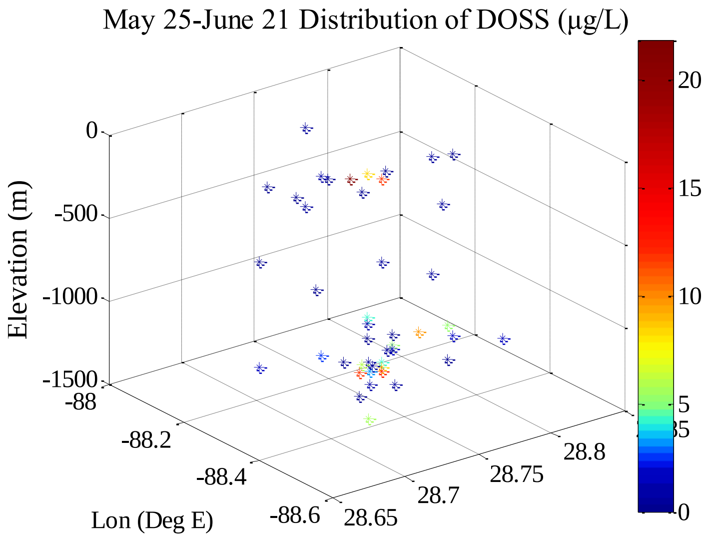

Figure 1. Distribution of DOSS during May 25 to June 21.

Methane, ethane and propane were selected in this study as they were of the highest abundance in the samples directly taken at the well head during the blowout (Reddy et al., 2012). Their distribution were shown in **Figures 2-4.** After the transported along with ocean current and biodegradation during June 11-June 21, methane abundance was still roughly 10 times of the abundance of ethane while ethane was around 2 times of propane. These proportions were agreed with the proportions directly collected at the well head (Reddy et al., 2012), indicating the transportation with movement of current was the primary process of gases and biodegradation was not substantial. The distributions of methane, ethane and propane, although of different magnitude, had very similar pattern that they concentrated around the well head which was commonly associated with single point source release. The distribution correlations showed the sequence of methane>ethane>propane. According to the results of Valentine et al. (2010), methane was hardly biodegraded while ethane and propane, especially propane were the primary drivers of microbial respiration. The distribution correlations were higher when the biodegradation rates of the analytes were lower indicating the DOSS was quite recalcitrant in the ecosystem.

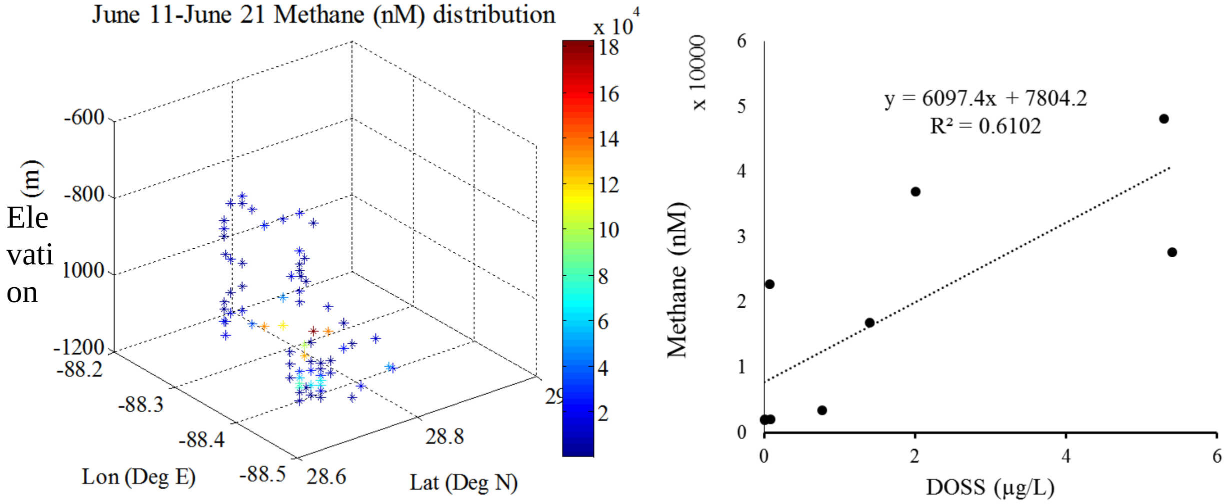

Figure 2. Distribution of methane during June 11-June 21 and its correlation with DOSS distribution

It was worth noting that the distribution correlation between methane and DOSS was slightly lower than the result ($R^2 = 0.80$, after excluding the abnormal data in cast #7) obtained by Kujawinski et al. (2011). This may be explained by the uncertainty generated with the interpolating process as Kujawinski et al. (2011) used the same water samples to measure of both DOSS and methane.

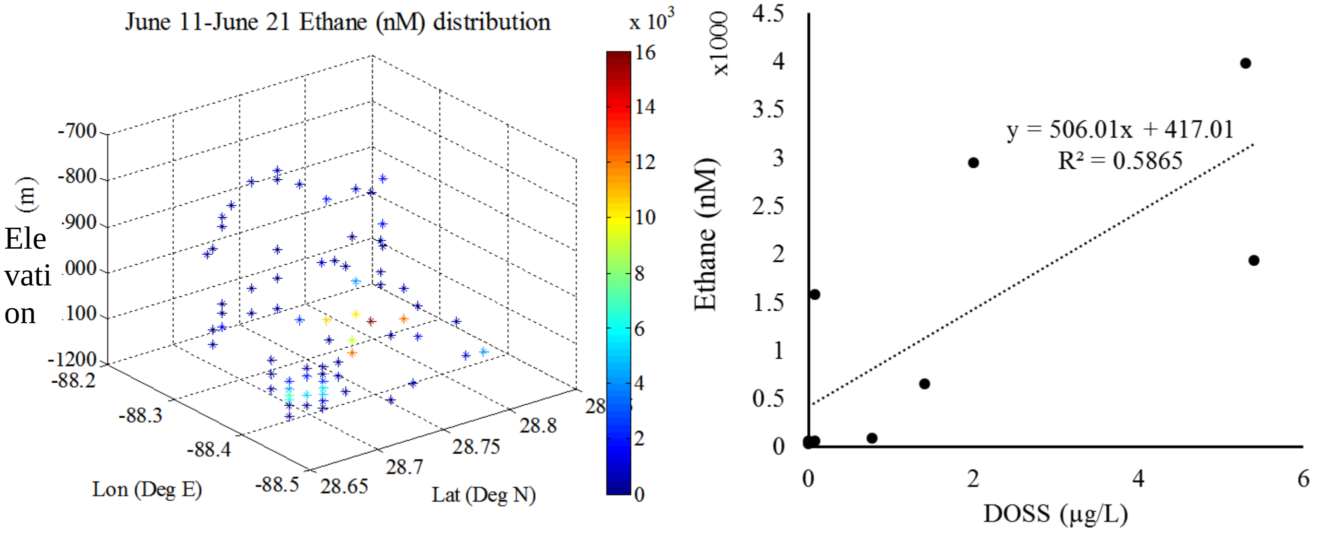

Figure 3. Distribution of ethane during June 11-June 21 and its correlation with DOSS distribution

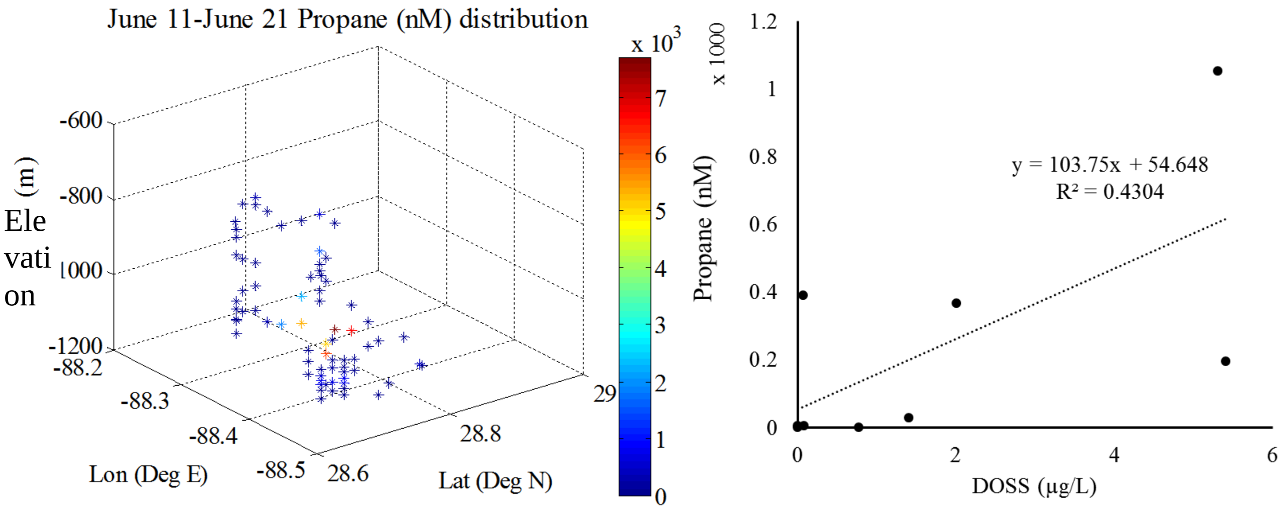

Figure 4. Distribution of propane during June 11-June 21 and its correlation with DOSS distribution

BTEX and PAHs were also included in the current study as they were primary components in the released oil (Reddy et al., 2012). The distribution of BTEX, 2-3 ring aromatic compounds, 4 ring aromatic compounds and total aromatic compounds were shown in **Figures 5-8**. The BTEX mainly concentrated around well head while higher molecular weight aromatic compounds tended to flow to the ocean surface. This difference could be partly attributed to the higher water solubility of smaller aromatic compounds. The solubility of BTEX range from 0.15 g/L to around 1.8 g/L at 20°C, whereas solubility of 4 ring aromatic compounds such as pyrene is around 0.135 mg/L (Aylward and Findlay, 1973). The lower solubility hydrocarbons had the higher tendency to flow to the air/water interface (Hoff et al., 1993). The concentration of BTEX was around 40 times of PAHs as shown in **Figures 5-7**. This proportion was much higher than the blowout point in the study of Reddy et al. (2012). This again could be attributed to the high solubility of BTEX which keep them in the water column, while the PAHs with low solubility formed the oil slick at the water surface.

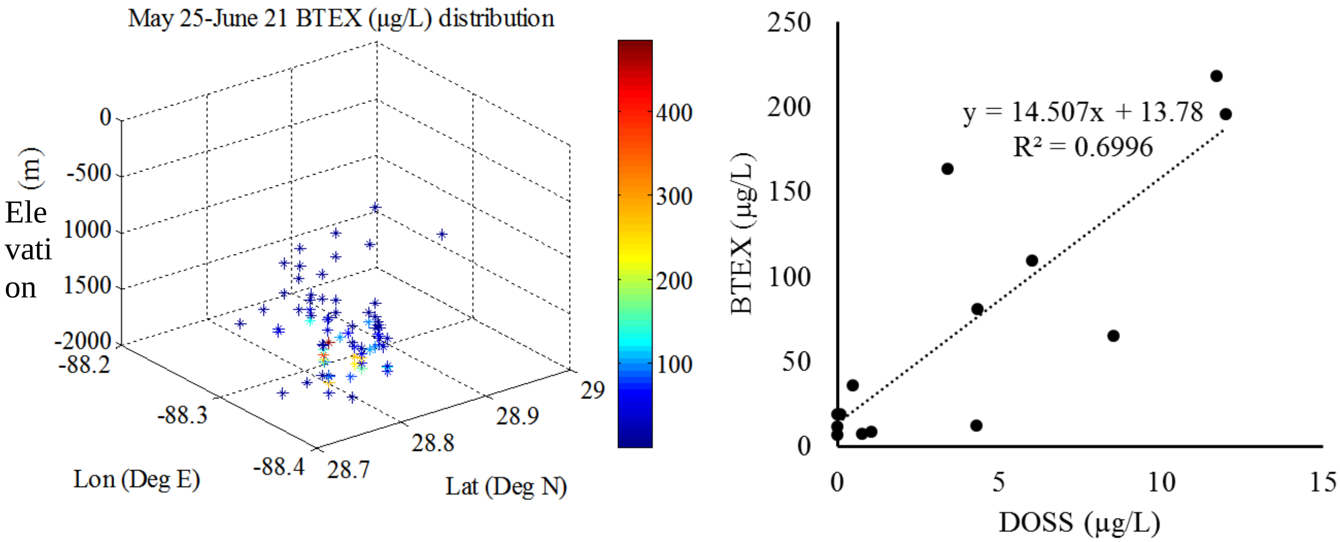

Figure 5. Distribution of BTEX during May25-June 21 and its correlation with DOSS distribution

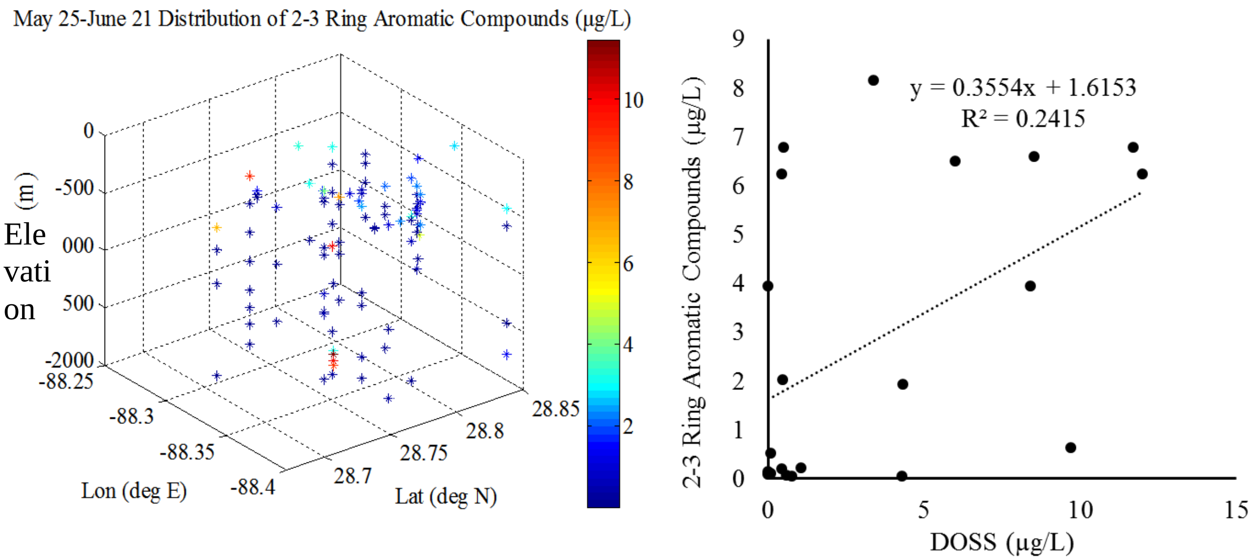

Figure 6. Distribution of 2-3 ring aromatic compounds during May25-June 21 and its correlation with DOSS distribution

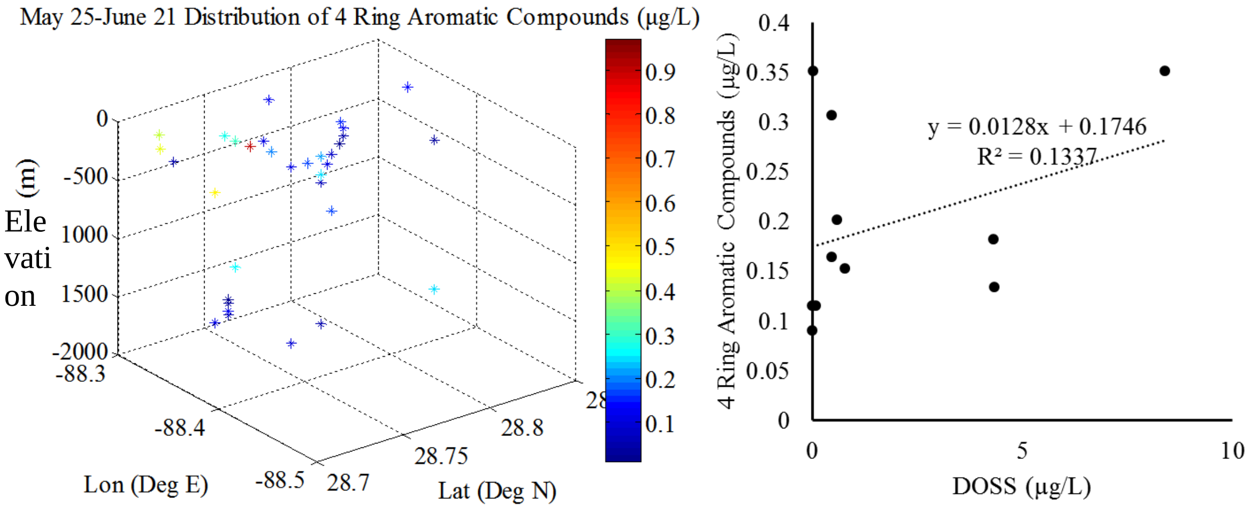

Figure 7. Distribution of 4 ring aromatic compounds during May25-June 21 and its correlation with DOSS distribution

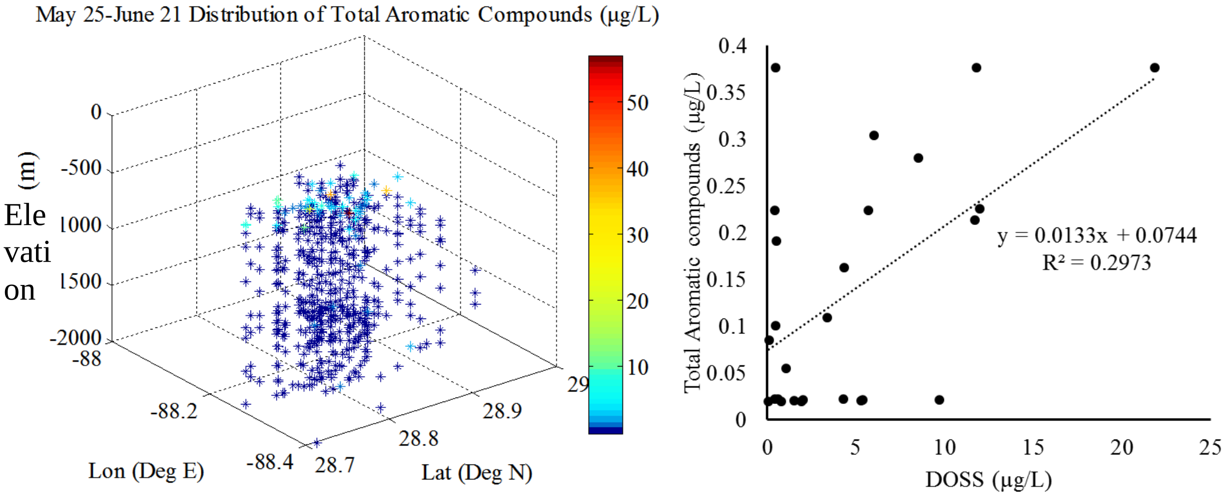

Figure 8. Distribution of total aromatic compounds during May25-June 21 and its correlation with DOSS distribution

Among different aromatic compounds, BTEX had the highest distribution correlation coefficient with DOSS. This value is even higher than three gases. When the molecular weight increased, the distribution correlation was decreased. The 4 ring aromatic compounds had the lowest distribution correlation (R^2=0.1337).

Moreover, 10 C alkanes, 14 C alkanes, 20 C alkanes and total alkanes were selected as alkanes were also the primary components of released oil (Reddy et al., 2012). The 10 C alkanes were evenly distributed in the ocean column with the concentration around 0.5 μg/L. The distribution correlation with DOSS was very low (r^2=0.0023). This may attribute to the overdose of Corexit dispersants. The small molecular alkanes were well dispersed and distribute evenly in the ocean column. The 14 C alkanes and 20 C alkanes concentrated at both well head and the water surface of the same latitude and longitude. The distribution correlations of alkanes increased when the higher molecular weight increased. Alkanes are hydrophobic and insoluble in water. Alkanes of 10 C and 14 C had low density (around 0.74).

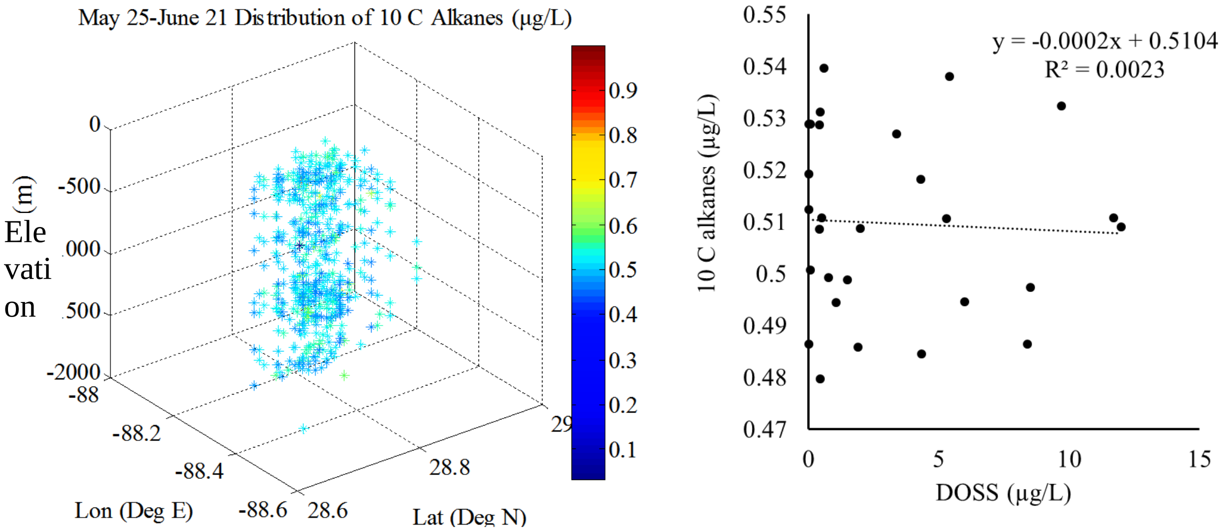

Figure 9. Distribution of 10 C alkanes during May25-June 21 and its correlation with DOSS distribution

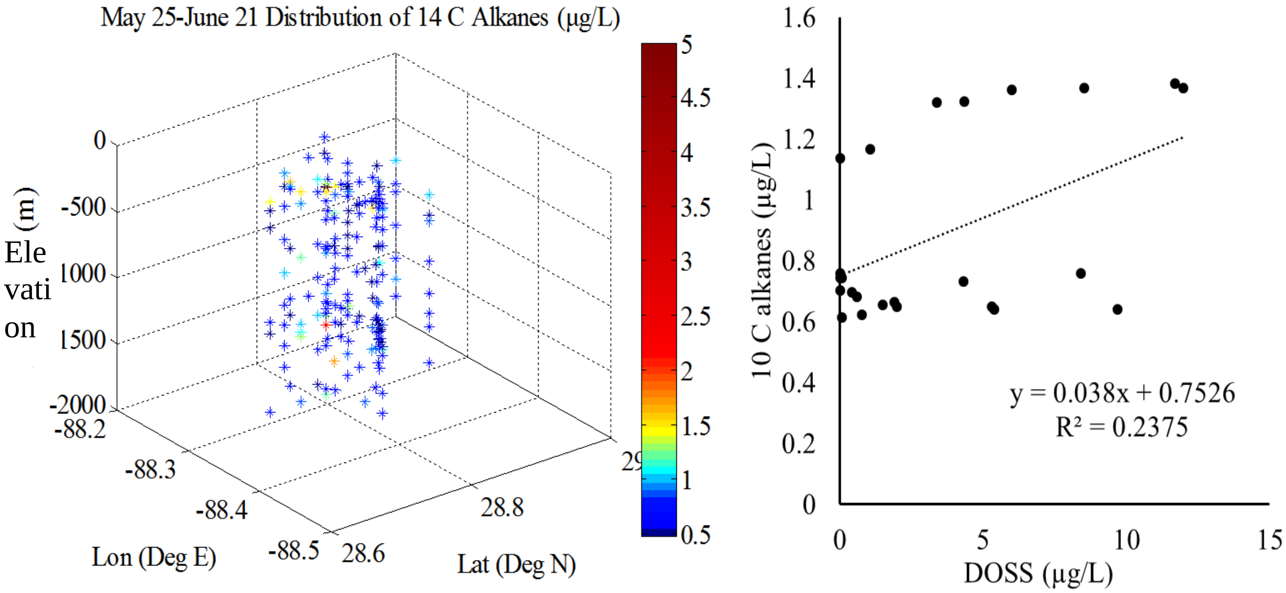

Figure 10. Distribution of 14C alkanes during May25-June 21 and its correlation with DOSS distribution

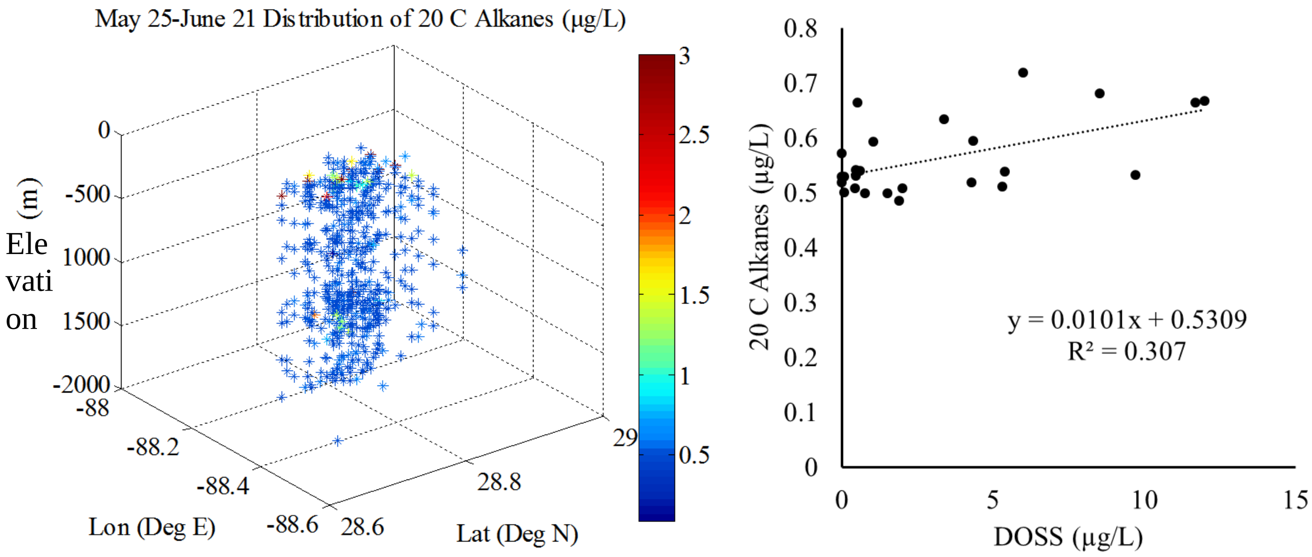

Figure 11. Distribution of 20C alkanes during May25-June 21 and its correlation with DOSS distribution

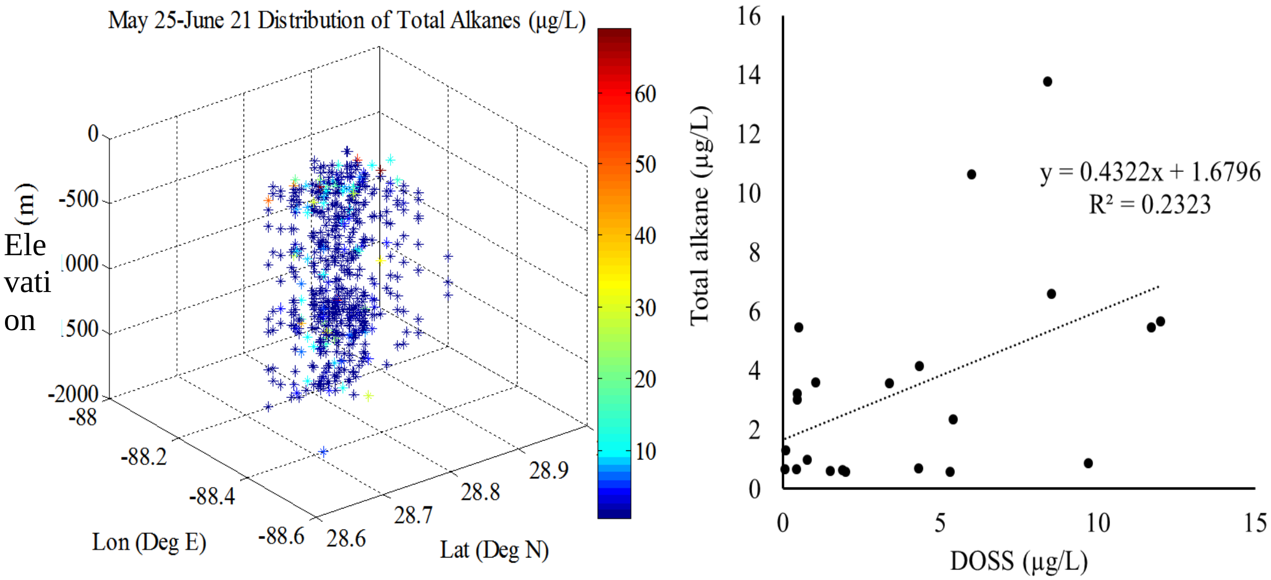

Figure 12. Distribution of total alkanes during May25-June 21 and its correlation with DOSS distribution

The correlation efficiencies Pearson's r, Kendall's tau, Spearman's ρ and their corresponding p values were listed in Table 3. Spearman's ρ and Kendall's tau are rank correlation coefficients. They measure the extent to which, when one variable increases, the other variable tends to increase. The increase dose not required to be represented by a linear relationship. These coefficients were less sensitive to non-normality in distribution (Kendall and Gibbons, 1990). As shown in Table 3, Methane and Ethane had higher Kendall's tau and Spearman's ρ than BTEX while their Pearson's r were lower than BTEX. These results indicated that the distribution of BTEX data had higher normality than Methane and Ethane. Pearson's r had the minimum insignificant correlations. By using Pearson' r, the sequence of distribution correlation with DOSS was BTEX > Methane > Ethane > Propane > Total Aromatics > 20 C Alkanes > 2-3 Ring Aromatics > 14 C alkanes > Total Alkanes > 4 Ring Aromatics > 10 C Alkanes.

Table 3. Correlation coefficients between DOSS and the analyzed parameters

		Pearson's r (*p* value)	Kendall's tau (*p* value)	Spearman's ρ (*p* value)
Gases	Methane	0.781*	0.686*	0.828*
		(0.013)	(0.011)	(0.006)
	Ethane	0.766*	0.686*	0.828*
		(0.016)	(0.011)	(0.006)
	Propane	0.656*	0.457*	0.584*
		(0.055)	(0.092)	(0.099)
Aromatics	BTEX	0.836*	0.573*	0.745*
		(0.000)	(0.005)	(0.002)
	2-3 Ring	0.491*	0.311*	0.45*
		(0.020)	(0.045)	(0.035)
	4 Ring	0.366	0.262	0.423
		(0.269)	(0.271)	(0.194)
	Total	0.545*	0.279*	0.382
		(0.004)	(0.047)	(0.054)
Alkanes	10 C	-0.048	-0.091	-0.142
		(0.809)	(0.501)	(0.471)
	14 C	0.487*	0.179	0.293
		(0.016)	(0.223)	(0.165)
	20 C	0.554*	0.286*	0.412*
		(0.004)	(0.047)	(0.041)
	Total Alkanes	0.482*	0.278	0.424*
		(0.023)	(0.071)	(0.049)

Conclusions

Between May 25 and June 21, in the ocean column of the Deepwater Horizon oil spill accident, interesting distribution correlations between different hydrocarbon compounds and the key Corexit ingredient: DOSS were found. The distribution correlations between different hydrocarbon flow and DOSS had the following sequence: BTEX > Methane > Ethane > Propane > Total Aromatics > 20 C Alkanes> 2-3 Ring Aromatics > 14 C alkanes > Total Alkanes> 4 Ring Aromatics > 10 C Alkanes based on the Pearson’s r coefficients. The higher distribution correlation indicated the similar behavior of the DOSS and the corresponding hydrocarbon compounds. This information would be beneficial for the understanding and predicting of the fate and behavior of Corexit dispersants in the ocean columns.

Acknowledgements

The authors would like to express the gratitude to Petroleum Research Newfoundland and Labrador (PRNL) and Research & Development Corporation (RDC) of Newfoundland and Labrador for their support.

References

Aylward G.H. and Findlay T.J.V. (1973). SI chemical data.

Benner R.A., El Said K.R., Jester E.L., Flurer R.A., Boyd B.L., Gamble B., Gratz S., Mulligan K.J., Heitkemper D.T. and Burrows D.G. (2010). Investigation of Corexit® 9500 Dispersant in Gulf of Mexico Seafood Species, US Food and Drug Administration.

Board of Ocean Studies (2005). Oil Spill Dispersants:: Efficacy and Effects, National Academies Press.

Corn M.L. and Copeland C. (2010). The Deepwater Horizon oil spill: coastal wetland and wildlife impacts and response, Congress Research Service.

FAO/WHO (1991). Toxicological Evaluation of certain food additives and contaminants, p. 30, Food and Agricultural Organization of the United Nations/World Health Organization, Geneva, Switzerland.

FAO/WHO (1995). Toxicological evaluation of certain food additives with a review of general principles and of specifications.

Goodrich M.S., Melancon M.J., Davis R.A. and Lech J.J. (1991). The toxicity, bioaccumulation, metabolism and elimination of dioctyl sodium sulfosuccinate DSS in rainbow trout (*Oncorhynchus mykiss*). Water Research 25(2), 119-124.

Gray J.L., Kanagy L.K., Furlong E.T., Kanagy C.J., McCoy J.W., Mason A. and Lauenstein G. (2014). Presence of the Corexit component dioctyl sodium sulfosuccinate in Gulf of Mexico waters after the 2010 Deepwater Horizon oil spill. Chemosphere 95, 124-130.

Hagerty C.L. and Ramseur J.L. (2010). Deepwater Horizon oil spill: Selected Issues for congress, Congress Research Service.

Hoff J.T., Mackay D., Gillham R. and Shiu W.Y. (1993). Partitioning of organic chemicals at the air-water interface in environmental systems. Environmental science & technology 27(10), 2174-2180.

Kendall M. and Gibbons J.D. (1990). Rank Correlation Methods, Oxford University Press.

Kujawinski E.B., Kido Soule M.C., Valentine D.L., Boysen A.K., Longnecker K. and Redmond M.C. (2011). Fate of dispersants associated with the Deepwater Horizon oil spill. Environmental science & technology 45(4), 1298-1306.

National Commission Final Report (2011). Deep Water, The Gulf Oil Disaster and the Future of Offshore Drilling (Commission Report)

National Resources Defense Council (2010). Gulf Coast Seafood Consumption Survey.

NODC (2014). the National Oceanographic Data Center, http://www.nodc.noaa.gov/deepwaterhorizon/specialcollections.html.

Reddy C.M., Arey J.S., Seewald J.S., Sylva S.P., Lemkau K.L., Nelson R.K., Carmichael C.A., McIntyre C.P., Fenwick J. and Ventura G.T. (2012). Composition and fate of gas and oil released to the water column during the Deepwater Horizon oil spill. Proceedings of the National Academy of Sciences 109(50), 20229-20234.

The White House Blog (2010). Daily reports from the Deepwater Horizon Incident Joint Information Center.

Valentine D.L., Kessler J.D., Redmond M.C., Mendes S.D., Heintz M.B., Farwell C., Hu L., Kinnaman F.S., Yvon-Lewis S. and Du M. (2010). Propane respiration jump-starts microbial response to a deep oil spill. Science 330(6001), 208-211.

Widger W.R., Golovko G., Martinez A.F., Ballesteros E.V., Howard J.J., Xu Z., Pandya U., Fofanov V.Y., Rojas M. and Bradburne C. (2011). Longitudinal Metagenomic Analysis of the Water and Soil from Gulf of Mexico Beaches Affected by the Deep Water Horizon Oil Spill.