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Investigating the Impact of the BP Deepwater Horizon Oil Spill on Trace Metal Concentrations in Bottom Sediments Retrieved from the Outer Continental Shelf (OCS) of Alabama and Western Florida, Gulf of Mexico

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Abstract The changes in the metal concentrations in sediments from the eastern Gulf of Mexico OCS can be explained by the presence of a new source for these metals. These metals were released from the damaged Macondo Well which resulted in the BP Deepwater Horizon Oil Spill during the spring of 2010. One-hundred and twenty sediment samples were collected during the fall months for the years 2008-2012 from the eastern OCS. The Tukey range test was used to compare measurement six metal concentrations between the relict sand deposits of the northern Gulf of Mexico OCS to the relict carbonate sediments off of western Florida OCS. Tests indicated that nickel (Ni), and lead (Pb) were significantly higher ($p<0.05$) in the seasonal average concentrations in the relict sand deposits after the spill. These higher concentrations are also reflected in the V to Ni ratio being at its lowest value in the relict sand (0.82) in the north, which is closer to the damaged well.

Keywords *Deepwater Horizon; Vanadium; Nickel*

1. Introduction

Between April 20 and July 15, 2010, approximately 686,000 metric tons of crude oil was accidently released from the British Petroleum (BP) Deepwater Horizon well located in the Gulf of Mexico (Figure 1; Hoch, 2010). The damaged wellhead released between 1,670 to 2,670 metric tons of crude oil per day (Johnson and Torrice, 2010). BP sprayed over 4,670 metric tons of chemical dispersants on the sea surface and injected 2,600 metric tons at the well head to alleviate the spread of crude oil slicks in the Gulf of Mexico (Kujawinski et al., 2010). The concentration of the dispersant as it was incorporated in the marine system was not controllable. The spray resulted in dispersant being delivered at various concentrations throughout the surface and the upper water column. These environments range from an open marine system to the ever changing coast line.

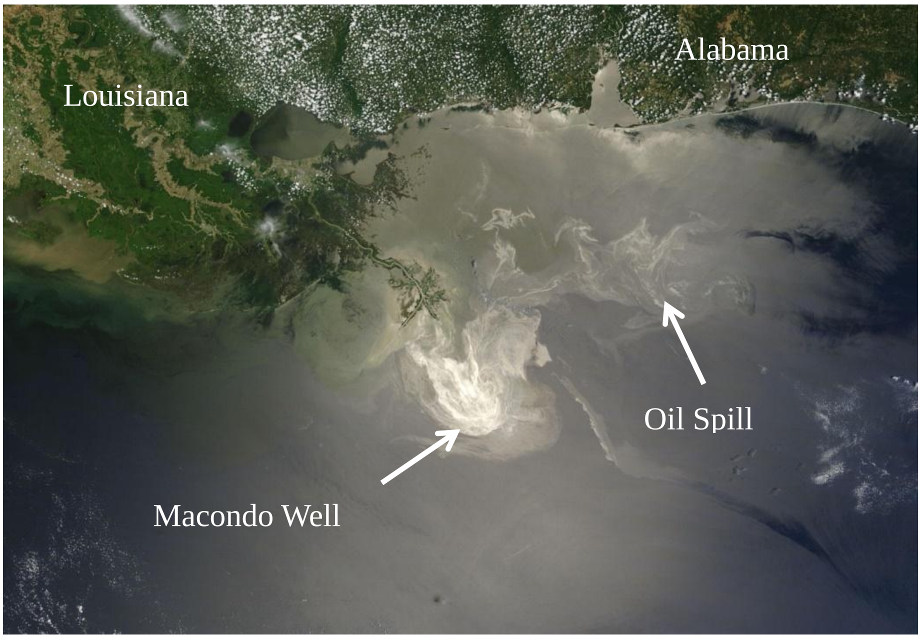

Figure 1: *NASA's Terra Satellite Image of the Oil Spill on May 24, 2010*

Liu et al. (2012) reported the following metals concentrations (μg g^{-1}) of concern for this report found in the crude oil released: V (0.2); Cr (9.4); Ni (1.5); and Pb (0.3). For V and Ni, Lui et al. (2012) found that the concentrations increased to 1.0 and 4.2 (μg g^{-1}) as the crude oil was degraded into oil mousse. Wise et al. (2014) measured Cr and Ni to range from 0.24 to 8.46 (μg g^{-1}) in crude oil from the wellhead, and oil from slicks on surface waters and tar balls from Gulf of Mexico beaches.

This study investigated the presence of trace metal concentrations found in sea bottom sediments along the relict sand deposits off of Alabama-Florida shelf and the relict carbonate sand off of western Florida (Figure 2). One-hundred and twenty sea bottom sediment samples were collected over a 5-year period (2008-2012) covering the time before and after the spill.

The study area is the OCS of the western Florida and Alabama. The shelf consists of an inner shelf (<40 m in depth), a middle shelf (40-100 m in depth), and the OCS (100-200 m in water depth). The 200-m bathymetric contour line is given in Figures 2 and 3. The shelf area is formed by an extensive carbonate platform along the west coast of Florida, and layers of lithogenous sediment north of Apalachicola Bay, Florida (Figure 2; Hine et al., 2003). To the west of the carbonate platform shelf (the study area) gives way to the continental slope which extends down to water depths of 1500 m and the Florida escarpment. To the east, the carbonate platform rises to form the inner shelf. By the early Cenozoic Period, the west coast of Florida became a drowned carbonate shelf (Hine et al., 2003). At this time, the shelf became deeper than the photic zone which resulted in a pelagic zone with reduced carbonate accumulation. This deepening occurred between depths of 100 and 200 m and extended over 100 Km between shelf and slope (Hine et al., 2003). Presently, the seafloor carbonates content ranges from 10% north of Apalachicola Bay to over 75% on the shelf south of bay (Balsam and Beeson, 2003).

By the middle Cenozoic Period, siliciclastic sediment eroded from the Southern Appalachian Mountains and was delivered to the inner shelf region (Balsam and Beeson, 2003; Hines et al., 2003).

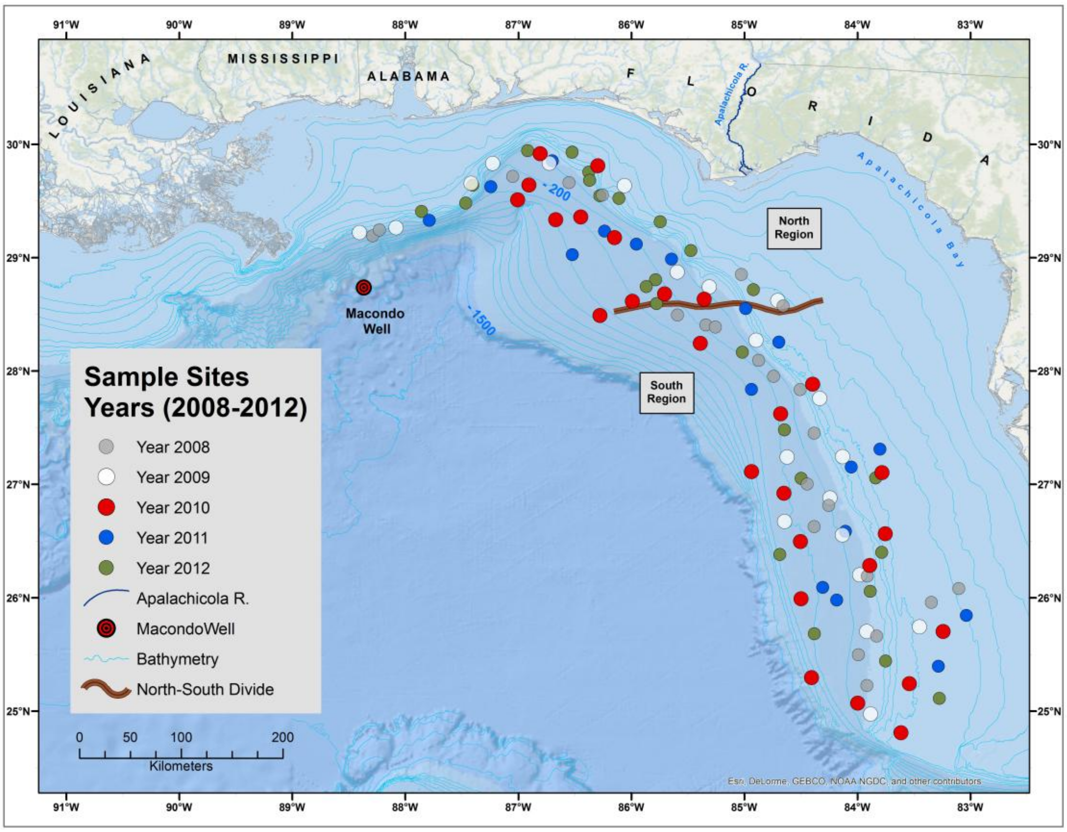

Figure 2: *Bottom sampling sites occupied during 2008 through 2012 along the Alabama and Florida outer continental shelves. The division between North and South Regions is also located*

Nineteen watersheds drain the western Florida coastline. The largest fresh-water outflow is from the Apalachicola River Watershed which drains 19,500 square miles of west-central Georgia, northwest Florida, and southeastern Alabama (Figure 2). Land use of this watershed is diverse and includes agricultural, residential, and industrial regions and the extensive Atlanta metropolitan area. Delivery of trace-metal laden sediment by this outflow to the inner shelf is likely. Sediment released is distributed by longshore currents in a northwest to a southeast direction parallel to the west Florida coastline. Quartz sand ridges parallel to the coast are formed by these currents and do not occur beyond 20 Km from shore (Figure 2; Balsam and Beeson, 2003; Hine et al., 2003).

Chemical analysis by the US EPA (Environmental Protection Agency) (2010) (Table 1) and studies by Steffy et al. (2013, 2014) (Table 2) indicate that V is lost during the decomposition process of crude oil, and Ni concentration is reduced to a lesser extent by these processes (Figure 3). Steffy et al. (2014) proposed that the retention of the Ni by the weathered oil and the resulting tarballs along the Alabama beaches indicate the Ni is being held tightly, probably by porphyrin rings as described by Yen (1975). Further studies of these metals have been advanced to recognize areal extent of the spilled oil’s impact on sea bottom sediment. This is found to have a significant impact on the active abyssal ecosystem (Landers et al., 2015; Nichols et al., 2014).

As elements, trace metals do not degrade. Once deposited on marine sediment as a component of a nonvolatile fraction of crude oil, the metals could remain after the organic fraction has been metabolized by microbes or otherwise decompose (Steffy et al., 2014). A complete list of metals found in MC252 spilled oil was listed by Liu et al. (2012).

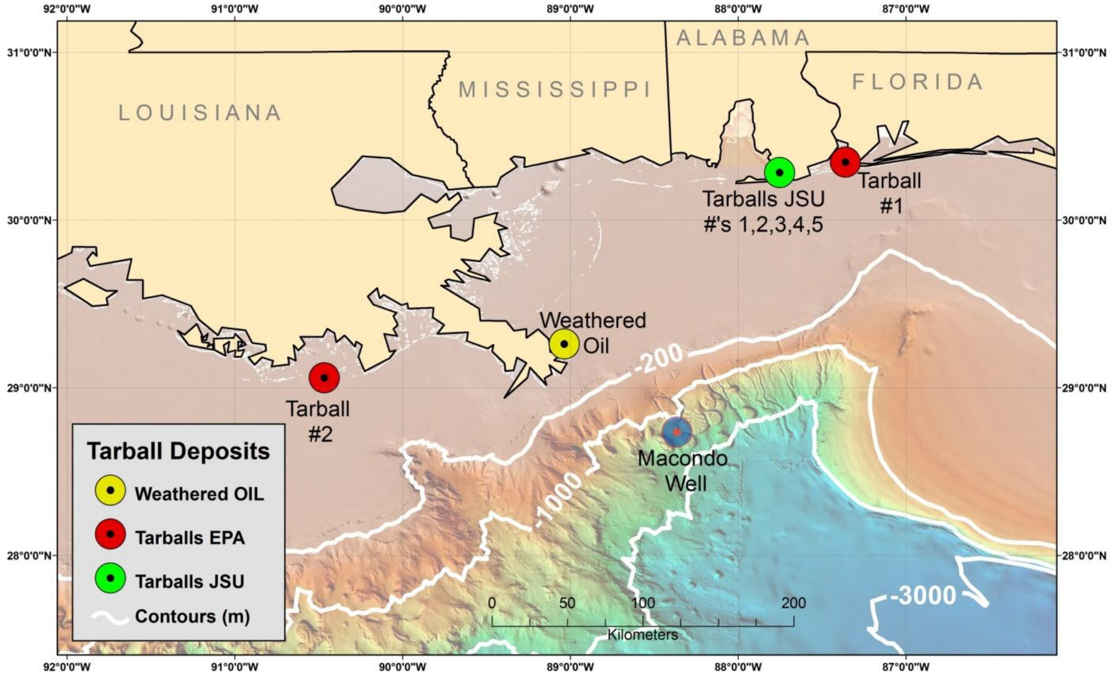

Figure 3: *Location of tarballs and weathered oil analyzed by US EPA (2010) and tarballs sampled by this study, both associated with the BP Deepwater Horizon oil spill released from the damaged Macondo well*

Table 1: *Trace metal content of tarballs and weathered oil measured in μg of metal per g of tarball or weathered oil associated with the oil spill (US EPA, 2010)*

Trace Metal	Tarball #1	Tarball #2	Weathered Oil
Cr	0.06	ND	ND
Ni	0.32	0.32	0.079
Pb	16.4	ND	0.240
Tl	0.07	ND	ND
V	0.20	ND	ND
Hg	0.06	ND	0.00024

ND indicates not detected

2. Methodology

The following methods were used to analyze for each of the 5-years' worth of sediment samples collected and analyzed by the authors. The methods are described previously by Steffy et al. (2014; 2013), and also are provided below.

Table 2: *Trace metal content of tarballs measured in µg of metal per g of tarball associated with the oil spill collected along the Alabama coastline by Steffy et al. (2014)*

Trace Metal	Tarball #1	Tarball #2	Tarball #3	Tarball #4	Tarball #5
Cr	ND	0.18 ± 0.32	0.45 ± 0.77	ND	ND
Ni	0.20 ± 0.18	0.38 ± 0.04	0.16 ± 0.28	0.10 ± 0.18	0.48 ± 0.55
Pb	0.64 ± 0.50	0.71 ± 0.18	0.56 ± 0.19	1.27 ± 1.36	0.59 ± 0.14
Tl	0.10 ± 0.09	0.14 ± 0.12	0.23 ± 0.11	0.06 ± 0.10	0.12 ± 0.11
V	0.12 ± 0.20	ND	ND	ND	ND
Hg	ND	ND	ND	ND	NA

ND indicates not detected. NA indicates not analyzed.

2.1. Field Methods

Sediment samples were collected in the fall during 2008-2012 as part of the NOAA (National Oceanographic and Atmospheric Administration) Small Pelagics Survey (Figure 2). One-hundred and twenty bottom samples were collected using a Shipek grab sampler operated from the decks of the NOAA R/V *Pisces* and R/V *Gordon Gunther*. The sediment is retrieved from the upper 10 cm (~0.32 foot) of the sea bottom. The sampler was returned to the ship's deck and a 40-ounce clear glass jar was filled with water-saturated sediment. The jar was labeled, sealed with a Teflon-lined lid and the sample placed in a 4°C walk-in cooler. Samples were transported to laboratory facilities at Jacksonville State University for processing and metal analysis (Steffy et al., 2013). The 2012 samples analyzed by this study supplements earlier data reported by Steffy et al. (2014).

2.2. Granulometric Analyses

A modified USGS method for granulometric analysis of marine sediment as described by Poppe et al. (2000) was used to measure the grain-size distribution. The modified method produced, a percent of the following fractions: gravel and larger size (>2mm), course sand (2mm–500µm), medium sand (500µm–250µm), fine sand (250µm–125µm), very fine sand (125µm–63µm), silt/ clay (<62µm), and the organic fraction. Data was statistically evaluated using Microsoft Excel and data plotted by a geographic information system was visually assessed to recognize areal trends.

2.3. Metal Analyses

Air dried sediment samples were subsampled into one gram triplicates and processed for metal analysis. Samples weighing approximately one gram were measured to ± 0.001 g and placed into acid washed 150 mL beakers for digestion. All reagents used in sample preparation and metal analyses were trace metal grade. Ultra-pure water (17 megaohm resistance) was used to prepare all solutions. All glassware was acid washed prior to each assay. Samples were digested using 15 mL of concentrated nitric acid, and further oxidized by the addition of 1 mL of hydrogen peroxide. The digested samples were diluted with 2 M sulfuric acid and filtered through a 45 mm filter into a 50 mL volumetric flask. The addition of 2 M sulfuric acid brought the total volume to 50 mL

2.4. Mercury Analyses

For Hg analysis, a 10 mL aliquot of the digested solution was pipetted into a BOD (Biological Oxygen Demand) bottle and 0.25 mL of nitric acid, 0.5 mL of sulfuric acid, 0.8 mL of potassium persulfate, and 2 mL of potassium permanganate were added. This solution was then heated for one hour at 95°C. Cooled samples received 1 mL of hydroxylamine prior to analysis. Standard Hg solutions were prepared from Fisher Certified Mercury Reference Solution, Lot No. 055614-24. Samples were analyzed for total Hg using US EPA Method 245.1, Manual Cold Vapor Technique (US EPA 1983). Hg analysis was conducted using a CETAC Quick Trace Mercury Analyzer M-6100 cold vapor atomic absorption Hg analyzer with an ASX-400 AutoSampler.

2.5. ICP Analyses

Digested sediment and tarball samples were submitted to Southern Environmental Testing, Inc. (Florence, AL) for ICP analysis using US EPA *Methods for Chemical Analysis of Water and Wastes*, EPA-600/4-79-020, revised May 1994.

2.6. Quality Control

Triplicates of each sediment sample were analyzed. All specimens were run in batches that included blanks (reagent and instrument) and spiked samples as part of the quality control for this study. All glassware was acid washed prior to each assay. All reagents used in sample preparation and metal analyses were trace metal grade. For Hg sample analysis, all samples were run in batches that included blanks (reagent and instrument), a five point standard calibration curve (standards of 0.0, 5.0, 10.0, 16.0, 24.0, and 32.0 mg/L with a linear correlation of 0.995 or better), and spiked specimens.

3. Results and Discussion

We hypothesize that the release of crude oil and the use of dispersants during the summer of 2010 associated with the BP Deepwater Horizon Well oil spill temporarily increased the trace metal concentrations in the sea bottom along the outer continental shelf of the Gulf of Mexico off of Florida and Alabama (Figure 1).

The study area is divided into North and South Regions with the boundary located on Figure 1. The boundary is based on several physical characteristics, which include: proximity to the damaged Deepwater Horizon well, water circulation pattern of the OCS, and known sea bottom sediment depositional pattern on the OCS. Figure 1 locates the damaged Macondo Well founded in 1,500 m water depth of the continental slope south of the Alabama – Mississippi state border. The surface oil spill depicted in Figure 1 indicates flow is clockwise along the OCS of Alabama and Florida. Long-shore currents of the inner shelf parallel the coast and flow clockwise as well (northwest to southeast). North of Apalachicola Bay, relict lithogenous sediment dominant the OCS of the North Region. South of Apalachicola Bay relict carbonate sediment the OCS of the South Region. This transition in the sea bottom sediment of the OCS from relict carbonate to relict lithogenous sediment defines the North-South boundary and is concurrent to the transition from carbonate to quartz sand of Balsam and Beeson (2003) and Distribution of Heavy Minerals (2015).

3.1. Granulometry

Granulometry data measured for 112 of the 120 sample sites from 2008-2012 collected from the OCS (Figure 1) have an average clay/silt content of 12.7 ± 9.3%, an average sand content of 76.2 ± 10.5%, an average gravel content of 8.4 ± 9.9%, and an average dissolvable organic content of 3.9 ± 4.2 %. According to the Folk (1954) classification scheme, the sediment would be classified as a gravelly muddy sand, as would most of the samples collected from the carbonate platform. Table 3 provides separate granulometry data for the South and North Regions. There is no significant statistical difference between the Regions. No distinction has been made in this study between hydrogenous, biogenous, or lithogenous components of the sediment samples. However, the geological history of the Floridian continental shelf (South Region) would indicate that the carbonate material is biogenous in origin (Balsam and Beeson, 2003; Hines et al., 2003). The South Region includes the Tyner et al. (n.d.) carbonate Middle Ground having an estimated overall carbonate depositional rate of 103 (g $CaCO_3/m^2$)/yr^{-1}. Most of the carbonate mass is from foraminiferal contribution. In contrast, the inner shelf of the South Region consists of a mixture of unconsolidated fine siliciclastic sand, and gravel size marine biogenic carbonate deposits < 3m (Hine et al., 2003). In Tampa Bay located on a coastal area of South Region, the Holocene accretion rate ranges from 1.4 to 4.1 mm yr^{-1} based on Pb-210 measurements (Trimble et al., n.d.).

The delivery of lithogenous sediment to the Florida OCS is unlikely because the longshore currents restrict the movement of sediment to the inner shelf being delivered by erosion of the adjacent continental margin. In contrast, The North Region covers the Alabama OCS which is more likely to receive lithogenous sediment delivered by the Mobile River (Emery, 1968), and by the Apalachicola River on the Florida OCS north of Apalachicola Bay (Figure 2). The eastern continental shelf of the Gulf of Mexico is a dynamic depositional system with reactivation and amalgamation occurring throughout its Holocene history (Anderson and McBride, 1996). Brooks et al. (2015) cite the sedimentation rate on the continental shelf at ~10 cm/1,000 yr northeast of the Deepwater Horizon well (North Region), and at ~17 cm/1,000 yr southeast of the well (South Region). They document rate based on Th-234 content could have received a pulse of sediment caused by a marine oil “snow” generated by the spill. This pulse of sediment is estimated to have been deposited within a 4-5 month period after the spill.

Table 3: *Granulometry results for the South and North Regions of the study area. Values are the mean percent of the sediment sample*

	South Region (n = 91)				North Region (n = 21)			
Year	**Granule**	**Sand**	**Silt/Clay**	**Organic**	**Granule**	**Sand**	**Silt/Clay**	**Organic**
2008	15.6	78.1	6.1	0.01	6.3	60.4	32.6	0.03
2009	10.7	78	4.6	6.7	33.1	63.2	3.6	0.1
2010	4.6	81.7	13.7	0.01	1.5	88.5	10	0.01
2011	0.2	88.7	9.8	6.3	0.4	77.8	20.2	8.7
2012	6.8	62.5	21	9.8	4.4	82.3	5.6	7.7
Mean	7.6	77.8	11.0	4.6	9.1	74.4	14.4	3.3
stdev	5.9	9.6	6.6	4.4	13.6	12.2	12.0	4.5

n is the number of sample sites

Steffy et al. (2013) reported that metal concentrations increases as grain size decreases. Metal concentrations also increase with ion exchange capacity increases, surface area increases and clay mineral content increases. There is no significant statistical difference between the regions in the silt/clay content of the sea bottom samples; however, there is a higher dissolvable organic content measured in the samples of the North Region.

3.2. Seasonal Mean Metal Concentrations Comparison

Seasonal mean (±standard deviation) metal concentrations for five metals present in sea bottom sediment samples collected from 53 of the 120 sites during 2008-2012 (Figure 2) are given in Table 4. Seasonal means are based on all samples collected and analyzed for the designated year. Seasonal mean metal concentrations of Ni, V, Pb, and Tl are at their highest concentrations in 2010. Seasonal mean sediment levels of V in 2010 were seven times as large as those from 2009 (Table 4), although this difference was not statistically significant due to the amount of variation among samples.

Seasonal mean sediment levels of Ni in 2010 were five times larger than those in 2009. Seasonal mean sediment levels of Pb in 2010 were six times larger than those in 2009. Seasonal mean sediment levels of Tl in 2010 were eight times larger than those in 2009. For Ni, V, and Tl mean concentrations for the years following 2010, showed lower concentrations.

Table 4: *Seasonal mean (± standard deviation) are shown for all metals. Values are measured in μg of metal per g of sediment*

Trace Metal	**Mean (± standard deviation)**	**2008**	**2009**	**2010**	**2011**	**2012**
Cr	8.01 ± 2.90	8.55 ± 4.73	5.66 ± 0.56	7.07 ± 3.86	8.58 ± 2.94	10.20 ± 0.17
Ni	6.07 ± 3.86	2.52 ± 1.13	1.93 ± 0.19	11.42 ± 5.42	7.49 ± 4.74	7.00 ± 0.09
Pb	3.48 ± 2.69	1.45 ± 0.40	0.71 ± 0.06	4.22 ± 2.17	3.09 ± 3.02	6.80 ± 0.17
Tl	0.24 ± 0.52	NA	0.06 ± 0.00	0.52 ± 0.85	0.14 ± 0.18	NA
V	7.27 ± 5.21	3.00 ± 1.93	2.08 ± 0.16	15.00 ± 7.05	7.07 ± 5.42	9.20 ± 0.25
Hg	0.15 ± 0.03	NA	0.03 ± 0.01	0.37 ± 0.01	0.05 ± 0.06	NA
Sites Sampled	53	10	7	12	18	6

NA indicates not analyzed

The seasonal mean concentrations (Table 4) are greater than for Ni, V, and Pb; and at the same order of magnitude for Cr present in the crude oil released from MC252 well as reported by Liu et al. (2012) and Wise et al. (2014). In comparison, the tarballs (Table 4) has less Cr and Ni than the crude oil, whereas the Pb reported by EPA (2010) exceeded both our measurements of tarballs and the crude oil value. It should be noted that Liu et al. (2012) and EPA (2010) did not report a standard deviation associated with their measurement. Wise et al. (2010) was not specific in the measurement and the standard deviation of the metals found. With respect to all three references, the lack of specific means and standard deviations prevented a statistical comparison.

3.3. Comparison of Seasonal Mean Metal Concentration Variations in North Region v. South Region

Figure 4 depicts seasonal mean concentrations for Ni, V, Pb, and Cr for the North and South Regions. These mean values are given as column ± standard deviations for each year. The 2010 means for Ni, V, and Pb appear to peak during 2010, which were sampled after the Deepwater Horizon Oil Spill. The Tukey range test was used to compare these four metal mean concentrations between the relict sand deposits of the North Region to the relict carbonate sediments of the South Region. Tests indicate that Ni, V, and Pb found in the North Region were significantly higher ($p<0.05$) than the South Region (Table 5).

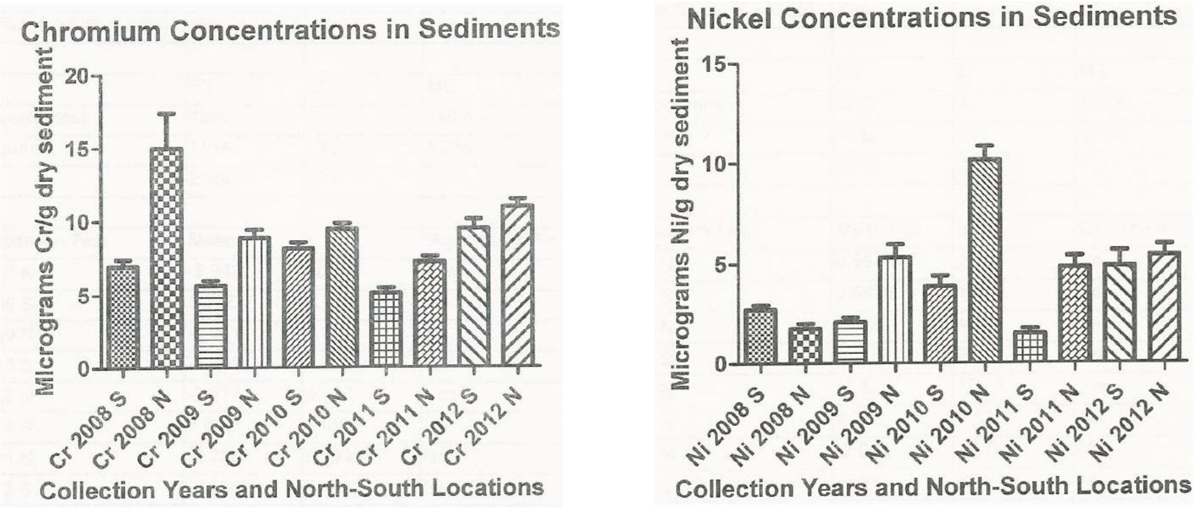

Figure 4(a): *Chromium*

Figure 4(b): *Nickel*

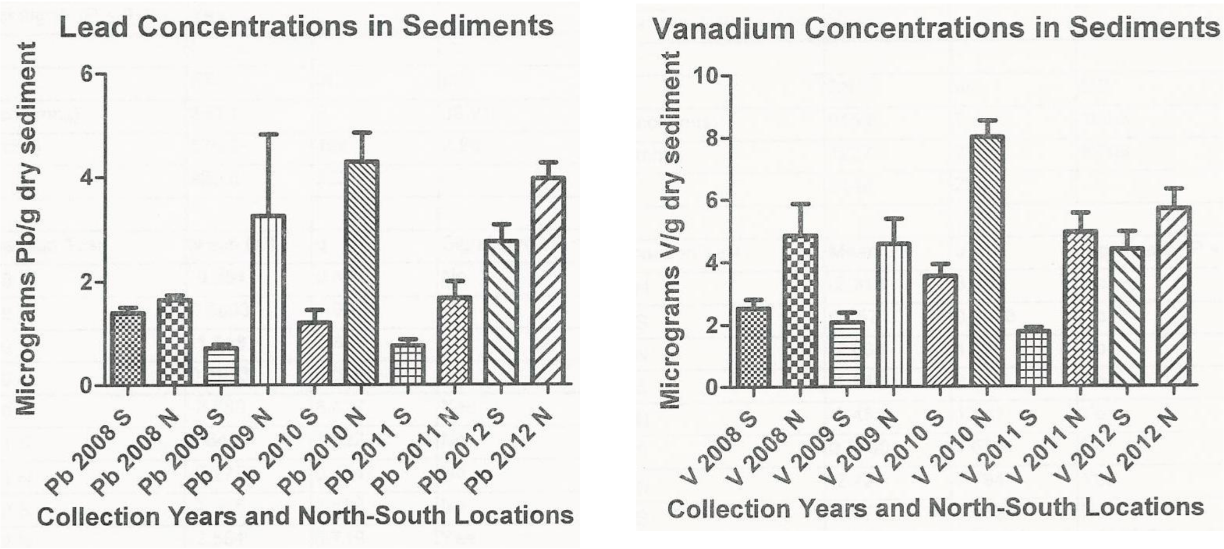

Figure 4(c): *Lead*

Figure 4(d): *Vanadium*

Figure 4: *Column plots of metal mean (± standard deviation) concentrations segregated for North and South Regions*

For all metals except for Pb in the study area, appear to have returned to pre-spill levels in the sea bottom sediment (Figure 4). These increases are statistical significant (Table 5). This natural recovery may be attributed to water currents or storms redistributing the metals present in the upper centimeters of sediment. The cause for the increasing level of Pb after the 2010 is unknown. It could indicate a new source of Pb is present, such as the effluence from Apalachicola Bay. The effluence and any accompanied sediment would be redirected by longshore currents in a northwest to a southeast direction parallel to the west Florida coastline (water depth <40 m), however. This needs to be investigated to confirm that a new source is present.

Table 5: *North vs. South Regions sea bottom sediment concentrations were compared for four metals during the fall of 2008-2012. Statistical significance was determined using one-way ANOVA with Tukey's multiple comparisons post-test*

	Year									
	2008		**2009**		**2010**		**2011**		**2012**	
Metal	**Mean Diff**	**q value**	**Mean Diff**	**q value**	**Mean Diff**	**q value**	**Mean Diff**	**q value**	**Mean Diff**	**q value**
Cr	-6.143	5.276*	-3.217	2.816*	-.9200	0.9444 ns	-1.728	2.078 ns	-1.468	2.605ns
Ni	0.911	0.7113 ns	-4.413	3.512*	-5.100	4.760*	-2.618	2.863 ns	-0.525	0.730ns
Pb	-0.2495	0.2987 ns	-2.536	3.095ns	-3.663	5.241*	-0.5499	0.9216 ns	-1.206	2.416ns
V	-1.246	1.091 ns	-4.690	5.246*	-3.728	3.901 ns	-2.549	3.125 ns	-1.299	1.929ns

Statistical significance indicated at * ($p < 0.05$), and "ns" is not significant

3.4. V-Ni Ratio Comparison of North Region v. South Region

We modified Yen's (1975) technique of fingerprinting crude oil with the V-Ni ratio by calculating V/Ni. Table 6 lists the average values of V-Ni ratios for each Region and for each year. For the 5 year time frame, the North Region has a lower average ratio of 1.09 ± 0.32 compared to the South Region's value of 1.54 ± 0.66. No statistical significance was determined to be present between the years when comparing North to South Regions, or when comparing North to South Regions for each year. These tests were conducted by using one-way ANOVA with Tukey's multiple comparisons post-test. For 2008, 2010, and 2011, the V to Ni ratios (Table 6) are higher, but not statistically, for carbonate sediment found in the South Region when compared to relict sand found in the North Region, which is closer to the damaged well. Also, in the North Region, the V-Ni Ratios are at its lowest value during 2010. This would suggest some of the trace metals measured in the 2010 samples were higher in concentration and derived, in part, from the oil spill.

Table 6: *Vanadium to Nickel ratio characteristic as it varies with year and area*

Year	**South Region (Relict Carbonate Sediment)**	**North Region (Relict Lithogenous Sediment)**
2008	2.61	0.91
2009	1.19	NA
2010	1.34	0.82
2011	1.66	1.09
2012	0.90	1.54
Mean	1.54	1.09
Stdev	0.66	0.32

NA indicates not analyzed

4. Conclusions

There appears to be a discernable rise and fall of trace metal concentrations in the sea bottom sediment in the eastern portion of the Gulf of Mexico OCS (Figure 4). The trace metals, Ni, V, and Pb, demonstrate this fluctuation during 2008-2012. We propose that the rise was caused by the presence of a new source of metals during the spring and summer of 2010 that being the Deepwater Horizon Oil Spill. The 2011 values approach pre-spill values, which represents natural remediation or dilution of metal concentrations in the sea bottom shelf sediment. The relict carbonate sediment of the South

Region has a statistically different V to Ni ratio compared to the relict sand of the North Region, which is closer to the damaged BP Macondo well.

On the west Florida carbonate shelf, the seafloor sediment seasonal concentrations of Ni and V, the two metals most strongly associated with crude oil, have a ratio that is significantly higher after the oil spill then before the oil spill in samples collected. This indicates that the spilled oil and the dispersants used to remediate the oil are new sources of trace metals to the Gulf of Mexico region.

The OCS is composed of gravelly muddy sand. Tarballs and weathered oil generated from the spilled oil that were analyzed from the Louisiana, Alabama, and Florida coastline indicate that Ni is being held tightly by the porphyrins in the oil while V tends to be lost. This would explain the trend measured in this study's North Region of the V-Ni ratio decreasing to its lowest value immediately after 2010 the Deepwater Horizon Oil Spill. Two years after the spill, the V-Ni ratio continued to increase.

Based on the limited number of sampling sites that have been processed to date, we believe that sediment concentrations of Ni and V could be indicative of an area north of Apalachicola Bay of the eastern Gulf of Mexico continental shelf contaminated by crude oil from the BP spill. As we continue to process sediments from additional collection sites, we will develop a better case for or against this hypothesis.

Acknowledgments

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