THE OSSA II PIPELINE OIL SPILL: NATURAL MITIGATION OF A RIVERINE OIL SPILL BY OIL-MINERAL AGGREGATE FORMATION

Kenneth Lee*, Patricia Stoffyn-Egli* & Edward H. Owens†

*Marine Environmental Science Division, Fisheries and Oceans Canada, Bedford Institute of Oceanography, P.O. Box 1006, Dartmouth, Nova Scotia, B2Y 4A2, Canada
(Tel & Fax: 902 426 7344; E-mail: leek@mar.dfo-mpo.gc.ca)
†Polaris Applied Sciences, Inc., 755 Winslow Way East, Bainbridge Island, WA, 98110, USA

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Fresh Water Oil Spills; Oil Spill Fate; Oil Dispersion; Oil Mineral Interactions

Abstract

Previous studies have documented enhanced rates of oil removal from marine sediments by physical dispersion and biological degradation processes following the formation of oil-mineral aggregates (OMA), microscopic particles of oil stabilised by fine minerals. In January 2000, approximately 29,000 bbl of crude oil were accidentally released from the OSSA II pipeline in the Bolivian Altiplano at a point crossing the Río Desaguadero. Mineralogical analysis of sediments from the Río Desaguadero basin revealed the presence of clay minerals known to readily interact with oil to form OMA. In support of laboratory tests that showed a significant amount of OMA formation in low salinity waters ($0.35^{o}/_{oo}$), OMA formation was observed when samples of Río Desaguadero water and sediment were mixed. Oil dispersion and enhanced biodegradation rates facilitated by rapid OMA formation after the spill incident may explain the oil fraction (27-37%) that was unaccountable in mass balance models that considered factors such as evaporative loss and oil recovered by clean up operations.

Introduction

Oil-mineral aggregates (OMA) are microscopic entities composed of oil and mineral particles that are stable over periods of weeks in water. Their formation may prevent oil spilled into the marine environment from recoalescing or adhering to surfaces (Lee *et al*., 1998; Lee and Stoffyn-Egli, 2001). Oil in OMA is more rapidly dispersed and weathered because the increased surface area enhances dissolution, evaporation and biodegration processes (Lee *et al*., 1997; Weise *et al*., 1999). In this regard, OMA formation has been identified as an effective natural oil spill mitigation process.

On January 30, 2000, the OSSA II pipeline, which crosses the Bolivian Altiplano, sustained a fracture at the trestle bridge where it crosses the Río Desaguadero (Fig. 1). An estimated 29,000 bbl of petroleum hydrocarbons were released into the closed basin system of the Río Desaguadero that connects Lago Titicaca (3,815 m elevation) with Lago Uru-Uru and Lago Poopó (3,685 m elevation). The spill coincided with the river's highest flood water level and impacted over 400 km of riverbanks and 500 km^2 of flooded lowlands (Owens, 2000; Henshaw *et al*., 2001). Fortuitously, the impact of the spill was confined within the Río Desaguadero basin. Total petroleum hydrocarbons (TPH) did not exceed the detection limit (50 mg/kg) in any of the 23 sediment samples collected at downstream river locations in February 2000 (Henshaw *et al*., 2001). Hydrocarbons were not detected in water and sediment samples collected from Lago Uru-Uru and Lago Poopó. Ecological damage was minimal; there were only a few reports of oiled birds or other wildlife (Wasson *et al*., 2000).

Analysis of stranded oil within the riverbank sediments confirmed that approximately 60% of the spilled oil was lost by combined evaporation, volatilization, and other weathering and degradation processes during the first six weeks. With additional data on the amount of surface oil remaining (<0.2%) and oil recovered (3-13%) at the end of clean up operations, it became apparent that a large fraction of the spilled oil remained unaccountable (27-37%, Owens 2000). On the basis of field observations, chemical analysis, mineralogical identification and laboratory experiments, it was hypothesized that the formation of oil mineral aggregates (OMA) may have effectively increased physical dispersion and oil biodegradation rates of the oil spilled into the Río Desaguadero (Bragg and Owens, 1994, Bragg and Yang, 1995; Lee *et al*., 1997; Lee *et al*., 1999; Owens, 1999). Controlled laboratory experiments were conducted with samples of oil, sediment, and water samples from the Río Desaguadero, as well as seawater, under various salinity conditions to test this hypothesis.

Materials and methods

Water, sediment and oil samples collected for this study are listed in Table 1.

Mineralogy

Mineralogy of the sediment samples and the suspended matter in the river water was determined by x-ray diffraction. Known amounts of sediment (70-140 g/l) were suspended in a 0.5% sodium metaphosphate solution and shaken for 2 hours (200 cycles/min in a reciprocating shaker) to disperse the clay mineral particles. Suspended solids in the river water sample were concentrated by settling and decanting before resuspension in the sodium metaphosphate solution. An aliquot of each suspension (0.75 ml) was air dried on a fritted glass slide. These oriented mineral mounts were left overnight in a chamber under partial vacuum with ethylene glycol to aid in the detection of expandable clay minerals (smectites). The samples were analyzed in a x-ray powder diffractometer (Siemens® D500 using cobalt $K\alpha$ radiation) between 2.5° and 29.5° 2θ. Identification of the minerals was done by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) mineral files.

Photomicroscopy

The suspended load of the river water sample was concentrated by settling overnight and decanting. A 30-μl aliquot of concentrated sample was deposited on a glass slide and covered with a glass slip. Six transects across the width of the cover glass (22 mm) and approximately 2.5 mm apart were scanned with a Leitz Ortholux microscope fitted with a combination of transmitted light and UV epi-fluorescence illumination (band pass excitation filter: 340-380 nm; reflection short pass filter: 400 nm; long pass suppression filter: 430 nm). U.V. epi-fluorescence illumination enables one to distinguish the oil phase because of the intense fluorescence characteristic of aromatic hydrocarbons. The non-fluorescent mineral particles were observed simultaneously by applying a small amount of transmitted light (Fig. 2).

Salinity

The salinity of an unpreserved Río Desaguadero water sample was determined to be 1.5‰ by the use of a hand held refractometer (Vista model A366ATC).

Suspended solid concentration

Sample # 2 (22.5 ml) was evaporated to dryness and weighed. The resulting value of 217g/l is very high, which explains why all residual oil samples contained a high proportion (50-80%, Henshaw *et al*., 2001) of sediment.

Experimental design

A laboratory study was initiated to determine if Río Desaguadero sediment and water would form aggregates with oil. The test oils were oil recovered from the site (sample #5, Table 1) and fresh OSSA II pipeline oil. The experiments included natural seawater (from Bedford Basin, Dartmouth, Nova Scotia) diluted to various salinity values with distilled water to investigate the influence of salinity on OMA formation. Experiments were conducted at 20-22°C, a temperature range similar to that at the time of the spill.

Mineral fines (20mg/l) were added to 100 ml samples of Río Desaguadero water (pure or diluted 10-fold) or diluted seawater (salinity values of 35, 3.5, 1.2, 0.7 and 0.35‰) in 250-ml Erlenmeyer flasks. The Erlenmeyer flasks were shaken for 10 minutes to allow the minerals to equilibrate with the test waters prior to the addition of 30±3 mg oil. The Erlenmeyer flasks were then shaken for four hours on a reciprocating shaker at a speed of 150 cycles/min (stroke length: 22 mm) to facilitate interaction of the oil with the mineral fines. A 20-ml sample was recovered and placed into a 22-ml glass vial overnight. Concentrated (2 to 20-fold) subsamples were recovered by aspirating the appropriate volumes from the center point of the liquid phase in the glass vial with a volumetric pipette, care being taken to preserve the floating phase gathered at the air/water interface and the sinking phase on the bottom of the vial.

The volume of oil in association with OMA was calculated by counting and measuring the size and shape of fluorescent particles (i.e. oil). Thirty microlitres of well-mixed sample were deposited on each of two counting chambers of an haemocytometer slide, prior to placement of the cover glass, as large mineral aggregates could hamper the normal sample delivery by capillary action. The slides were analyzed with a Leitz TAS$^+$ image analysis system coupled to an Orthoplan U.V. epi-fluorescence microscope (excitation filter: 450-490 nm; reflection short pass filter: 510 nm; suppression filter: 515 nm) with a computer-controlled, motorized stage. As the microscope was used in fluorescence mode only, there was strong contrast between the dark background and the fluorescent oil. A 25× objective was used (detection limit is then 3.5 μm) to count and measure all fluorescent particles in 56 fields of view (approximately 0.1 ml of sample). Three counting chambers were counted for replicate measurements.

The oil volume of each fluorescent particle was calculated by the method of ‘ultimate erosion’: fluorescent particles are “eroded” (stripped of their surface pixel layers) sequentially, and their size calculated on the basis of the number of erosions necessary to make them disappear. Their volume is then calculated based on a sphere of similar diameter. The total volume of oil within OMA in the sample has been expressed as mg of oil (oil density = 0.80 g/ml for OSSA II oil). The results were plotted in Fig. 3 as percent of the oil added to each Erlenmeyer flask.

Results and Discussion

Conditions that favour OMA formation were present in the Río Desaguadero at the time of the spill, including the availability of fine clay mineral particles and oil of a reasonable viscosity range that could be readily dispersed under the prevailing energy regime. The Río Desaguadero was in its annual flood stage coinciding with the rainy season (December to March). Flow speed on the order of 2.5 m/s combined with a shallow river bed (less than 3 m) to create strong turbulence throughout the water column —standing waves and boils were observed — that kept large amounts of sediment in suspension, making the water highly turbid. Oil viscosity was not a limiting factor in the formation of OMA. To improve flow properties, the heavy crude oil in the OSSA II pipeline had been diluted with a kerosene-range petroleum product. It was concluded that this petroleum hydrocarbon mixture was rapidly dispersed into small droplets (precursors in OMA formation) by the turbulent river flow following release.

Sediments of the riverbank are predominantly comprised of smectite (swelling clay), mica (including illite), kaolinite, quartz and feldspars. The load of suspended solids in the river water was composed of the same minerals, but enriched in clays and depleted in quartz and feldspars (Fig. 4), since clays are usually more fine-grained than quartz and feldspars, and thus more easily resuspended. The clay minerals identified in the Río Desaguadero are known to readily form OMA with a variety of oil types (Lee *et al*. 1998).

Microscopy revealed very few OMA in the three water samples collected from the Río Desaguadero in March and April 2000, 6 to 9 weeks after the spill. Those observed were droplet aggregates ranging in size from 2-20 μm in diameter (Fig. 2a). In one sample with a high abundance of suspended clay and silt, some fluorescent mineral particles were also observed. These appeared to be the result of residual oil adhering to the surface of mineral particles. That mineral auto-fluorescence was not a contributing factor was borne out by laboratory experiments in which no fluorescent particles were observed in a sample of unoiled Río Desaguadero sediment dispersed in filtered deionized water. The paucity of OMA in water samples recovered 6 to 9 weeks after the spill was not surprising when one considers that the spilled oil was transported 350 km in four days (Wasson *et al*., 2000).

A few mg of a sample of residual oil collected from the riverbank (Sample #5, Table 1) were shaken in river water containing unoiled Río Desaguadero sediment. Although most of the residual (weathered) oil did not disperse because of its high viscosity, small droplet OMA could be observed in the sample at the end of the shaking period. Moreover, some small particles of the sediment-rich oil liberated by shaking were observed floating in the water (Fig. 2b).

The experiment using the fresh OSSA II pipeline oil resulted in abundant OMA that included some large (>50 μm) buoyant particles (Fig. 2c). Image analysis indicated that approximately 40% of the oil formed OMA (Fig.3) during four hours of shaking river water with a sediment load value three orders of magnitude lower than that of the Río Desaguadero in flood condition. These results strongly suggest that OMA were immediately formed when the spilled oil was released into the water.

To date, OMA occurrence has been reported only in seawater, and it has been suggested that high salinity is necessary for OMA formation (Bragg and Yang, 1995). However, this hypothesis has not been tested. When the brackish waters of Río Desaguadero were diluted 10-fold with distilled water (to 0.15 g/l), negligible amounts of OMA were formed. The quantity of oil incorporated into OMA at various salinities is shown in Fig. 3. Although OMA were observed at all salinities (0 to 35 ‰) with OSSA II pipeline oil, they were much less abundant in distilled water. OMA-bound oil reached a maximum at a salinity range of 0.7 to 1.2 ‰, very close to the value of 1.5 ‰ measured in Río Desaguadero water. The elevated ionic content for waters of this inland system may be attributed to the fact that the flood plain is a closed system highly influenced by evaporation. The fact that the amount of OSSA II oil in OMA is lower in river water than in diluted seawater of similar salinity (1.2 ‰) may be due to the different elemental composition of dissolved solids in the Río Desaguadero as compared to seawater.

Conclusions

Abundant oil-mineral aggregates were generated from OSSA II pipeline oil and Río Desaguadero sediment and water samples under simulated field conditions (temperature, water turbulence). Laboratory tests with a reference sample of the crude oil blend from the OSSA II pipeline confirmed that the salinity of the Río Desaguadero water was sufficiently high to promote OMA formation. In addition, mineralogical analysis of suspended and riverbank sediments revealed an abundance of clay minerals, especially smectite, which have been proven to easily interact with oil to form OMA (Lee *et al.*, 1998; Wood et al., 1998; Lee and Stoffyn-Egli, 2001).

Evidence from this study suggests that OMA formation occurred in the Río Desaguadero immediately after the spill. It is hypothesised that OMA formation was effective in reducing the environmental impact of the spilled oil by promoting widespread dispersion and dilution of the oil in the flood plains and enhancing natural biodegradation rates. Until now, reports on OMA formation and its environmental significance in oil spill mitigation have been associated with studies in marine waters. The Río Desaguadero study has now provided information on the potential for OMA formation and its environmental significance following an inland oil spill.

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Table 1 Samples used in this study

Sample ID	Sample matrix	Date collected	Sample Site	Analytical Procedure
# 1	Oil residue in sediment	15-Mar-2000	Riverbank, Site B	Mineralogy
# 2	Sediment-rich water*	15-Mar-2000	Channel near stranded oil, Site B	Microscopy, mineralogy, sediment load
# 3	Surface river water*	15-Mar-2000	Mid-channel, Site B	Microscopy
# 4	Unoiled sediment	15-Mar-2000	Exposed part of channel, Site B	Mineralogy
# 5	Sediment-rich oil	15-Mar-2000	Stranded oil patch, Site B	Lab testing for OMA formation
ET-1	River water	08-Apr-2000	Site A	Microscopy, mineralogy, salinity
ET-2	Sediment	08-Apr-2000	Site A	Mineralogy
PNC-0-93A	Fresh oil	21-Apr-2000	Pipeline, above break	Lab testing for OMA formation

*samples fixed with mercuric chloride to prevent bacterial degradation of oil.
Site A: 17°32’59” S; 67°42’02” W; Site B: 17°45’50” S; 67°28’20” W (Fig. 1).

FIGURE CAPTIONS

Figure 1. Location of the January 30, 2000 oil spill on the Río Desaguadero, Bolivia. A and B are the sites where the samples for this study were collected.

Figure 2. Epi-fluorescence micrographs of oil-mineral aggregates (the bright areas are fluorescent oil particles): **A** - Droplet oil-mineral aggregate found in Río Desagadero water; **B** - sediment-rich oil particle generated from the weathered residual oil; **C -** oil-mineral aggregates observed in laboratory tests with Río Desaguadero water and sediment, and fresh OSSA II pipeline oil.

Figure 3. Percentage of total OSSA II pipeline oil incorporated into OMA at various salinities in laboratory experiments.

Figure 4. X-ray diffractogram of suspended particulate matter in Río Desaguadero water. Smectites are a major component of the suspended clay minerals.

Figure 1

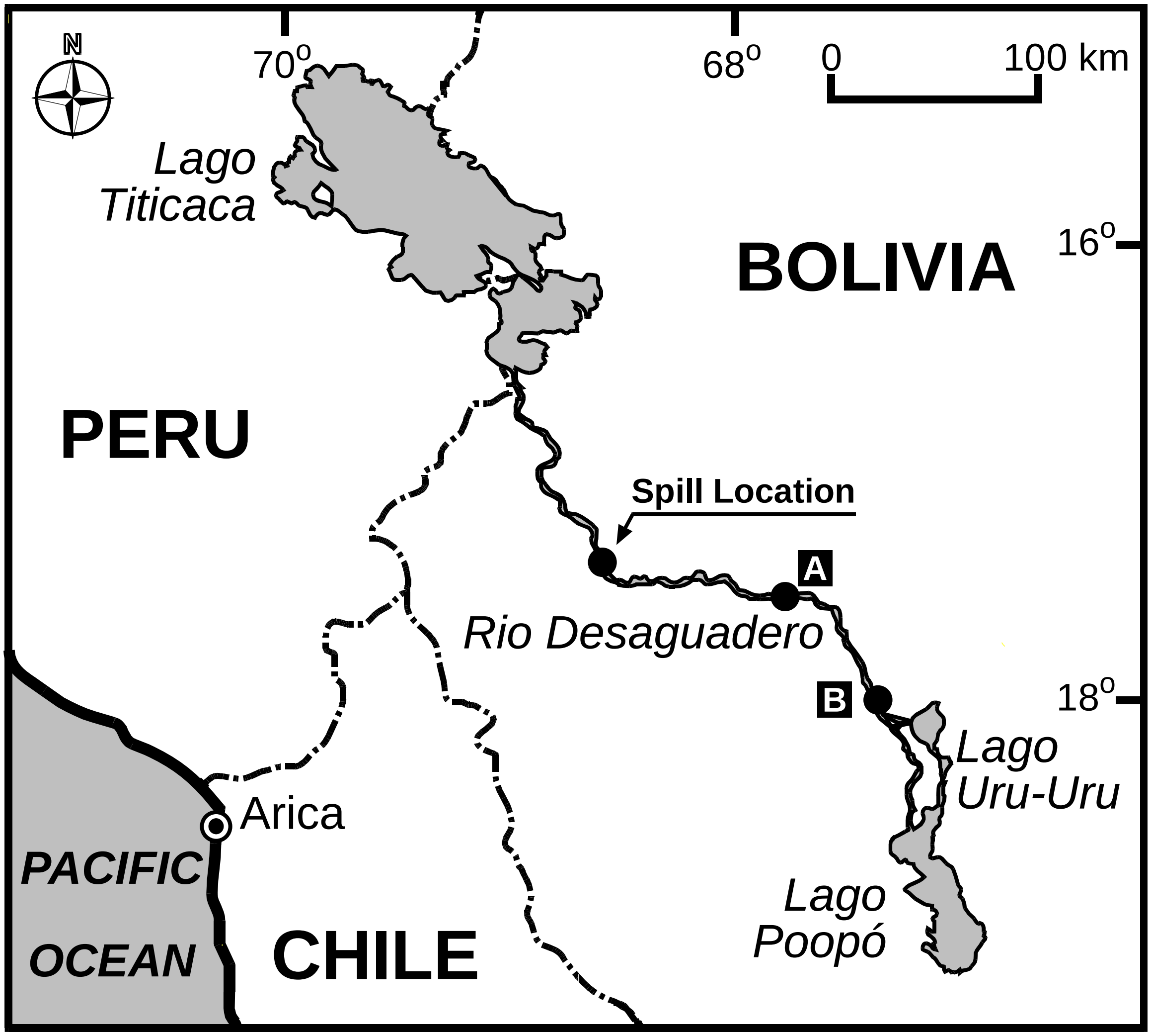

N
70°
68°
0
100 km
Lago
Titicaca
16°
BOLIVIA
PERU
Spill Location
A
Rio Desaguadero
B
18°
Lago
Uru-Uru
Arica
PACIFIC
OCEAN
CHILE
Lago
Poopó

Figure 2

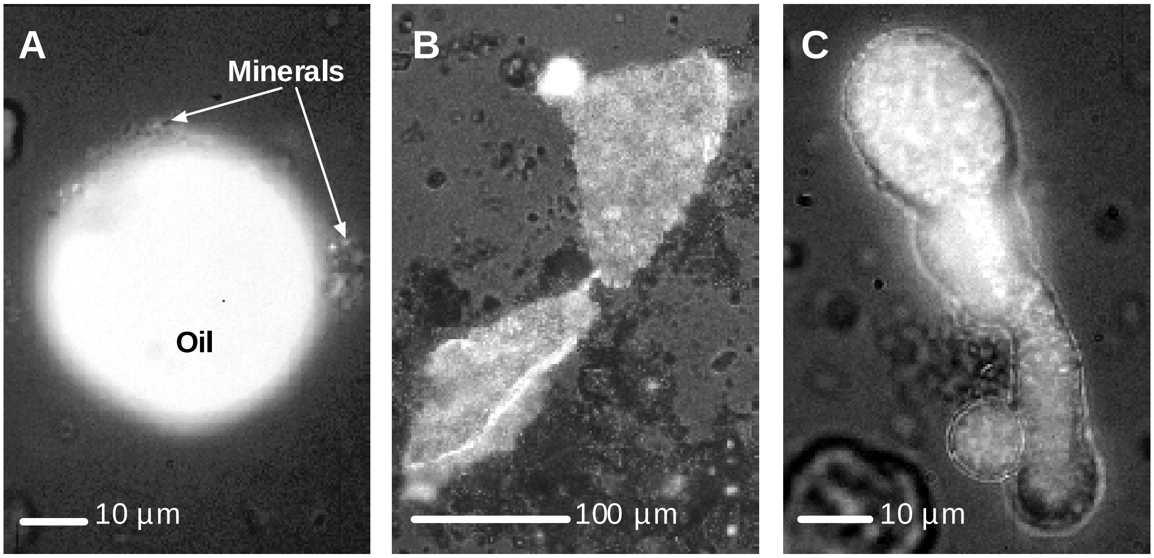


Figure 3

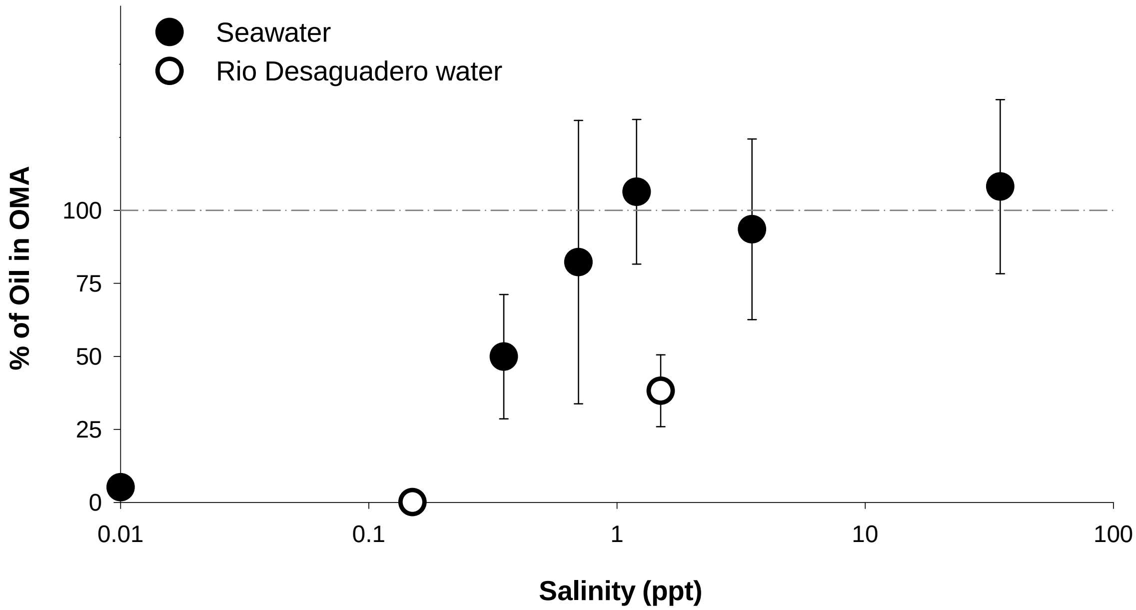
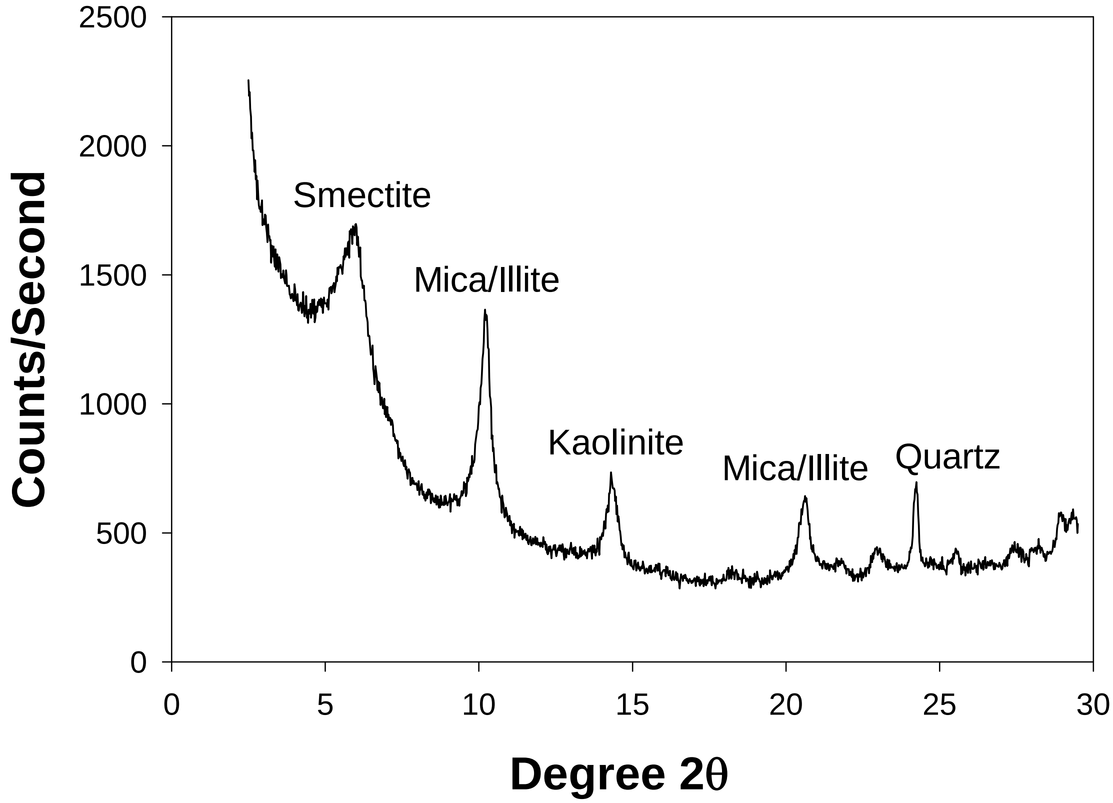

Seawater
Rio Desaguadero water
% of Oil in OMA
100
75
50
25
0
0.01
0.1
1
10
100
Salinity (ppt)

Figure 4


2500
2000
1500
1000
500
0
Counts/Second
0
5
10
15
20
25
30
Degree 2θ
Smectite
Mica/Illite
Kaolinite
Mica/Illite
Quartz