

Summer Research Academy Symposium

Friday, August 2, 2013
9:00 am

J. Bennett Johnston
Health and Environmental
Research Building
Room 111A

Sponsored by:

National Science Foundation
and

Gulf of Mexico Research Initiative



EDEB 2013 INTERNS



CMEDS 2013 INTERNS

Programme

9:00 am Opening Remarks

Oral Presentations

| | Presenter(s) | Mentor |
|----------|----------------------------|--------------------------------|
| 9:05 am | Lawrence Aiken | Paul Russo, PhD |
| 9:20 am | Rosalyn Kent | Florastina Payton-Stewart, PhD |
| 9:35 am | David Galin | Louis Thibodeaux, PhD |
| 9:50 am | Julie Kaiga | KiTani Parker-Johnson, PhD |
| 10:05 am | Allen Huang | Krishnaswamy Nandakumar, PhD |
| 10:20 am | Anna Naiki and Gina Nguyen | Syreeta Tilghman, PhD |
| 10:35 am | Break | |
| 10:45 am | Kelly O'Quinn | Michael Benton, PhD |
| 11:00 am | Brittini Summers | Patience Obih, PhD |
| 11:15 am | Mary Osetinsky | Vijay John, PhD |
| 11:30 pm | Carolina Rodriguez | Meredith Sattler, PhD |
| 11:45 pm | Tuan Tran | Henry Ashbaugh, PhD |
| 12:00 pm | Joyce Ward | Vijay John, PhD |
| 12:15 pm | Kristen Wollman | Noshir Pesika, PhD |
| 12:30pm | Karry Wright | James Donahue, PhD |

There will be a reception immediately following the oral presentations.

-All are invited-

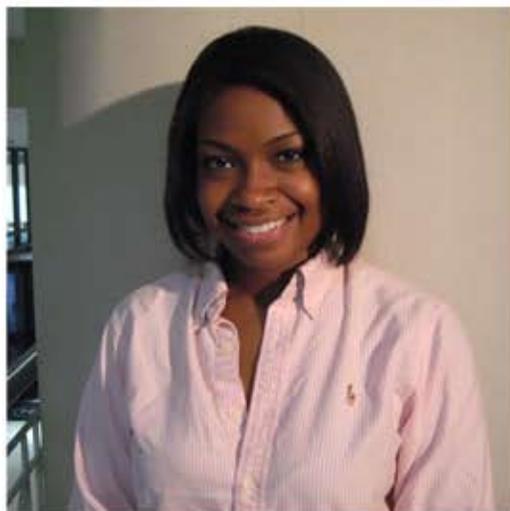


Novel Colloid Characterization

Lawrence R. Aiken, Jr, Xujun Zhang, and Dr. Paul S. Russo,
Louisiana State University, Department of Chemistry, Baton Rouge, LA

Crude oil is used extensively in the creation of plastics and fuels. When an oil spill occurs, the ecosystem can be severely affected, as evidenced most recently by the Deep Water Horizon incident. As oil is both immiscible and less dense than (salt) water, it tends to sit on top and spread out very quickly. To combat this, a class of proteins called hydrophobins may be used to contain the oil particles. From the two existing classes of hydrophobins, two of them are involved in this project, H* (a proprietary material) and cerato-ulmin. Hydrophobins, like H* and cerato-ulmin, are known as hydrophobic, meaning that they will repel water. Conversely, oil particles will stick to the hydrophobin and may be encapsulated. This research project aims to assess the potential of hydrophobins to clean oil, particularly as a supplement or replacement for synthetic dispersants. Hydrophobins and other natural surfactants have been interacting with petroleum leaked from rifts in the sea floor for eons. It is only logical to wonder how effective nature's solution to oil spills is compared to the ones we humans have devised. The research to be described involves refractometry to find the dn/dc (change in refractive index with concentration) of various solutions, such as H* and water. Testing for the refractive index will allow for the calculation of a particle's/compound's equivalent molecular weight, which will allow the researcher to determine if a hydrophobin that contains air (or oil) can be stabilized for a period of time sufficient for collection and proper disposal. If hydrophobins such as H* or cerato-ulmin make microscopic bubbles when agitated in the presence of air and gases, the refractive index of the bubble should be less than that of solution. A problem is that large bubbles may obscure the scale of the refractometer. This can be solved by waiting until they clear, as only a small negative shift is needed between the sample and control. Refractometry studies began with a better-characterized protein, bovine serum albumen, which has hydrophobic properties.

Finding the dn/dc of various samples of hydrophobins has shown them to be stable. Images from a microscope also show oil (as well as air) can be contained inside a hydrophobin membrane. Also, it has been learned that changes in pressure do not affect the overall structure when the bubble contains oil, e.g. with a decrease in pressure, there is no expansion, and with an increase in pressure, there is no contraction. In the case of bubbles containing air, results show that the bubble is both compressible as well as expandable, but the bubble retains its overall integrity.



Synthesis of Capsaicin Analogs as Anticancer Agents for Breast and Bladder Cancer

Rosalyn Kent, Dr. Ravi Subramanya, and Dr. Florastina Payton-Stewart
Xavier University of Louisiana, Department of Chemistry, New Orleans, LA

Breast cancer is the second leading cause of cancer death among women in the United States. According to the American Cancer Society, it is estimated that in 2013, there will be 232,340 new cases of invasive breast cancer diagnosed in women, and 39,620 women will die from breast cancer. Studies have shown that in contrast to the United States there is a history of lower incidences of breast cancer seen in women of Asian descent. Research shows that Asian women tend to have a daily regimen enhanced with fruits and vegetables. These studies prompted our lab to study the effects of the phytochemical known as capsaicin and its effects on breast and bladder cancer.

Capsaicin, N-(4-hydroxy-3-methoxybenzyl)-8-methylnon-6-enamide, is the primary pungent ingredient in red peppers, which possesses anti-carcinogenic, anti-inflammatory and chemo-preventive properties. Previous studies show that capsaicin induces significant growth arrest and apoptosis in human breast and bladder cancer cell lines in vitro with no significant effect on normal breast epithelial cells. We hypothesize that structural modifications of capsaicin will lead to effective anti-cancer agents. These structural modifications will also lead to the identification of important structural activity relationships (SAR) of the analogs and their biological activity. Capsaicin analogs are synthesized using the Schotten-Baumann reaction for the acylation of amides from amines and acid chlorides. Following the synthesis the analogs are purified by recrystallization and column chromatography. Finally, the analogs are analyzed using thin layer chromatography (TLC), gas chromatography-mass spectroscopy (GC-MS) and nuclear magnetic resonance (NMR).

Preliminary data has shown that we were able to synthesize, purify and chemically analyze the capsaicin analogs effectively. Capsaicin analogs are effective at inhibiting the growth of bladder cancer cells. Future work is to unravel the mechanism of action of capsaicin analogs on bladder cancer and evaluate their biological effects on breast cancer cells.



Solute Sinking of Orthodichlorobenzene and Benzene in Water with and without Dispersant

David James Galin and Dr. Louis J. Thibodeaux

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During an oil spill, the chemicals in the oil can stay suspended in the water and can the more soluble components dissolve, causing the heavier and less soluble components to sink. The objective is to perform a laboratory experiment of deep-sea spill initiating event and develop the model of oil-water with and without dispersant to understand dissolution process, the role of dispersant, and the fate of oil. The apparatus used was an 18 gallon glass container with a circulation pump, an inverted petri dish suspended in the water with a glass collection cone underneath the dish. A solution of orthodichlorobenzene and benzene was dyed red and injected under the dish and the time was recorded for the first drops to fall. The droplets with dispersant fall quicker as the bond strength constituents and interfacial tension of the oil is weakened. A theoretical model of the sinking time is in development as more results are collected. This shows how dispersants alter the dissolution process with oil and cause the heavier residuals to fall faster, which could minimize the oil at the surface of a spill and keep the less soluble components at a lower marine level.



MMP-7 Expression is Enhanced by Noncancerous Microenvironment of Triple Negative Breast Cancer Cells

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²Xavier University of Louisiana, Department of Psychology, New Orleans, LA
³Xavier University of Louisiana, College of Pharmacy, New Orleans, LA

Purpose. The progression of breast cancer towards metastatic disease remains a poorly understood area of investigation. Among the most metastatic of breast cancers are those with the triple negative phenotype. Recently in my laboratory, we discovered that noncancerous breast epithelial MCF-10A cells secrete factors into their media that stimulate growth of triple negative breast cancer (TNBC) cell line MDA-MB-231 much more robustly than normal growth medium supplemented with fetal bovine serum. More interesting was the observation that these factors not only promoted growth and migration of TNBC in vitro, they also substantially increased invasion of the MDA-MB231 cells. Even though exosome research represents a nascent area of investigation, we propose to use this approach to uncover novel mechanisms that drive the progression of TNBC and better understand the role of the external microenvironment of TNBC cells in tumor proliferation, migration, and invasion. **Methods.** Bioassays such as alamar blue and transwell migration were used to evaluate proliferation and migration of triple negative breast cancer cells were performed using conditioned media. Super arrays were used to evaluate gene differentiation in the different growth conditions and Western blot analyses were performed on selected molecules. Samples from both MDA-MB-231 and MDA-MB-468 were evaluated. **Results.** The proliferation data indicated that conditioned media (CM) significantly enhanced the growth of both MDA-MB-231 and MDA-MB-468 cells when compared to the growth of the cells. Migration was increased both MDA-MB-231 and MDA-MB-468 cells when treated with CM compared to regular media. Super array analyses indicated that MMP-7 increased by nearly 4 fold and 3 fold, respectively, in MDA-MB-231 and MDA-MB-468 cells in CM media compared to regular media. Western blot demonstrated that MMP-7 had increased expression in both MDA-MB-231 and MDA-MB-468 cells treated with CM compared to regular media. **Conclusion.** Taken together, these data indicate that factors secreted by the noncancerous microenvironment of the TNBC cells enhance the expression of MMP-7 that increases the proliferation and migration, thus promoting metastasis.



The Effects of Surfactant on Droplet Dynamics and Jet Breakup Length

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Hypotheses and Statements: Experiments were carried out to analyze the effect of surfactant addition to the oil phase on the dynamics of a single oil droplet rising through a stagnant water column. The surfactant concentration in the dispersed phase was varied and the change in droplet dynamics was observed in terms of the deviation in the rise velocity and aspect ratio.

In another aspect of this study, experiments were conducted to address the effects of surfactant on jet breakup phenomenon. Also, the influence of mass transfer on jet breakup length has been investigated for toluene-acetonitrile-water system.

Methods and Results: To observe how surfactant concentration inside oil droplets affected the dynamics, three different sized nozzles were used inside of a tall tank full of water. The nozzles were placed at the bottom of the tank and oil was pumped droplet by droplet and was recorded using a high speed camera. Corexit-9527 was used as the dispersant and was dissolved into the crude oil. Dispersant-to-solvent ratio was varied between 0 and 0.005. It was observed that droplet size and rise velocity both decreased as dispersant to solvent ratio increased.

Analysis of the effect of mass transfer on jet breakup involved injection of an organic phase that consisted of toluene and acetonitrile (soluble component) into the quiescent water column. Solutions were prepared in varying concentrations of acetonitrile by volume percent from 0%-40%. Results showed that as solute concentration increased, maximum jet breakup length decreased. Some results showed a shift: that is, as solute concentration increased, the maximum jet breakup length was reached at lower flow rates.

For the experiment involving the effect of surfactant concentration on jet breakup length, the organic mixture was pure toluene and was introduced into the water column using a fine tip glass nozzle connected to a syringe pump. The surfactant (SDS, sodium dodecyl sulfate) concentration in the continuous phase was varied in the range between 0 and 750 PPM. Results appear to show that as surfactant concentration is increased in the continuous phase, jet breakup length also increases. In the above experiments, a high speed camera was used to analyze the jet breakup lengths.

Conclusion: To summarize, increasing surfactant concentration lowers rise velocity and makes the droplets flatter (aspect ratio increases). Also, it was observed that increasing surfactant concentration increases jet breakup length, and the experiments involving mass transfer revealed that as solute concentration in dispersed phase increased, maximum jet breakup length tended to decrease.



Glyceollin I Suppresses Cellular Motility in Letrozole Resistant Breast Cancer.

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Department of Basic Pharmaceutical Sciences, New Orleans, LA

Postmenopausal women with early-stage estrogen-dependent breast cancer are generally treated with antiestrogens (i.e., tamoxifen) or aromatase inhibitors (AI) (i.e., anastrozole and letrozole). However, acquired resistance remains a major clinical obstacle, thereby creating a critical need to identify mechanism(s) of resistance and ultimately developing potential therapeutic options. As such, many naturally occurring agents, particularly soy containing compounds, such as glyceollins, have recently gained interest as potential therapeutic breast cancer agents. Of these compounds, several appear to directly affect tumorigenesis of estrogen-dependent and estrogen-independent breast cancers.

In order to examine AI resistance, a letrozole-resistant breast cancer cell line (LTLT-Ca) was developed in the Brodie laboratory. These cells undergo adaptive changes such as activation of the MAPK signaling pathway, increased expression of HER2 and IGF1R, decreased expression of aromatase and ER α leading to estrogen-independence. Previously our lab identified a proteomic signature that is associated with hormone independence, enhanced cell migration and invasion. The objective of this study was to examine the effect of a previously characterized novel phytochemical, glyceollin I, on protein expression of letrozole resistant breast cancer.

Glyceollin I treatment resulted in a 60% reduction in colony formation of LTLT-Ca cells. Subsequent migration and invasion assays demonstrated more than a 50% decrease in the motility of the LTLT-Ca cells. Moreover, targeted gene expression arrays confirmed glyceollin I treatment caused 3-fold decrease in Snail and Caveolin expression as well as additional genes involved in epithelial-to-mesenchymal transition (EMT). We identified several proteins implicated in cell motility that were significantly altered including beta catenin, claudin 1, and TGF β 2. A western blot analysis was performed to confirm the respective expression alterations of these EMT marker proteins, as well as to analyze the expression of other stem cell marker proteins including CD24, CD44, and Zeb1.

Taken together, our study demonstrated the potential of glyceollin I to decrease cell motility and may represent a novel approach in the treatment of metastatic, endocrine resistant breast cancer.



A PCR Based Assay for Bioplastic Production from Cyanobacteria

Kelly R. O'Quinn, Courtney E. Lane, and Dr. Michael G. Benton
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Currently, petroleum is the main source for the raw materials needed to synthesize plastics. However, due to environmental and sustainability concerns associated with petroleum usage, alternative polymer production methods are being sought. Bioplastics are an excellent alternative to petroleum-based plastics since they are both sustainable and carbon neutral. They also have similar mechanical properties to traditional plastics, such as those made from the biopolymer polyhydroxybutyrate which have similar melting point and glass point temperatures to plastics produced from polypropylene. However, bioplastics are manufactured using materials derived from living organisms, called biopolymers, rather than from petroleum. Some species of cyanobacteria produce granules of the biopolymer polyhydroxyalkanoate (PHA) which can be extracted to make bioplastics. Cyanobacteria are photosynthetic prokaryotes that use atmospheric carbon dioxide to obtain energy. Bioplastics are not yet replacing traditional plastics because their production costs are much higher than that of petroleum-based plastics, often due to carbon feedstock. Because cyanobacteria fix atmospheric carbon, the cost of carbon feedstock is lessened. However, they generally show low yields of PHA. Since there are potentially more than one million species of cyanobacteria, it is likely that some species are capable of producing PHA at the level required to make bioplastics more economical. However, the process of screening millions of species for the desired PHA production levels is daunting. To find all PHA producers we have developed a PCR based assay to test a large number of cyanobacterial species simultaneously to more quickly determine which species are most likely to be PHA producers. Because the process of fully analyzing and optimizing the PHA accumulation characteristics of different species is time intensive, we would like to effectively weed out those which cannot produce PHA early on. This rapid screening process was developed on two positive controls and one negative control. It was then tested against two strains of cyanobacteria in which there was no genomic information available. The test has worked on these two unknown strains and can now be implemented for use in other strains in which DNA information is unknown.



Investigation into the Antidiabetic Activity of Blueberry (*Vaccinium arctostaphylos* L) Via Inhibition of α -glucosidase

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Diabetes is the 7th leading cause of death in the United States. It is associated with many complications such as retinopathy, neuropathy and nephropathy. Insulin and oral hypoglycemic agents are the main stay in the control of type 2 diabetes. Current therapeutic strategy for the control of postprandial hyperglycemia also includes the inhibition of α -glucosidase resulting in delay of carbohydrate digestion to absorbable monosaccharide. Drugs like acarbose and miglitol with similar mechanism of action have been introduced into the market, but they have side effects. Some studies have shown that blueberry possesses antidiabetic activity. This project seeks to evaluate the mechanism of antidiabetic action of blueberry. Our hypothesis is that blueberry reduces hyperglycemia by inhibiting α -glucosidase. The inhibitory effect of different concentrations of aqueous extract of blueberry on α -glucosidase was studied in vitro. The inhibition was carried out in a 96 well plate and measured with Thermo Scientific® Multiskan spectrometer. Our result showed that blueberry inhibited α -glucosidase (IC₅₀ of 32 mg/ml). In summary, blueberry aqueous extract inhibits α -glucosidase in our system. The observation made in this project may go a long way to furnish information for strategies for better therapeutic management of diabetes. However, further study is needed to accomplish this.



Novel Hydrophobically Modified Chitosan PLGA Particles Tethered to Liposomes

Mary Osetinsky, Jaspreet Arora, Lek Boonkaew, Dr. Vijay John

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PLGA is an established and well-known drug delivery vehicle. PLGA nanoparticles can be fabricated through nanoprecipitation; during this process the surface of the PLGA particles can be coated with polymers. Chitosan is a biopolymer that is known to be mucoadhesive. Hydrophobic groups were attached to the chitosan backbone by covalently bonding the hydrophobes to the amine group of the chitosan monomer. We then coated the PLGA particles with the hydrophobically modified chitosan (HMC). This coating enables the particles to attach more easily to cells due to the mucoadhesive properties of the HMC. In addition, the hydrophobes on the surface of the particle can facilitate hydrophobic interactions with other drug delivery vehicles such as liposomes. PLGA particles were combined with the HMC by first forming an oil in water emulsion and then evaporating off the oil phase. The resultant hydrophobically coated PLGA particles were imaged using confocal microscopy, which confirmed that coating of HMC did take place. Further, the attachment of liposomes was fluorescently visualized using confocal microscopy. Reaction conditions including HMC concentration, pH, the addition of PEG, and PLGA concentration were studied in order to establish a size control of the particles and to optimize the attachment of liposomes. This system can potentially open up doors for a novel method of compounded drug delivery which exploits the advantages of both PLGA and liposomes as drug delivery vehicles such as increased loading of hydrophobic drugs in the PLGA particles as well as hydrophilic drugs in liposomes.



Louisiana's Future Coast: Visualizing Land Loss, Dynamic Natural Systems and Settlement Patterns

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Coastal Louisiana's current land loss crisis is a result of the interaction between human resource extraction, human settlement patterns, and dynamic natural forces, many of which are largely invisible in space and time. Recently, in response to dire future predictions, communities have started to question the sustainability of their long-term planning strategies, to challenge their understanding of habitation on fast changing wetland ground, and to explore more resilient options. This research seeks to develop a dynamic four-dimensional visualization and design tool that may assist communities and designers make more informed development decisions in the face of climate change and land loss. We hypothesize that the importance of visualization is increasing as we observe changes at increased rates. This hypothesis leads us to our research question:

Is it possible to develop a modeling methodology that is simple enough for designers to build and utilize in the visualization and communication of dynamic landscapes and anthropogenic processes through a continuous time/space frame?

Development is subject to major natural forces that we have little control over, and, in the process of modeling Louisiana's dynamic landscape, it was first necessary to investigate the behaviors of natural dynamic forces and their resulting processes. To do this, we examined existing ecological systems models (ECMs) and translated them into parametric modeling protocols utilizing the Grasshopper plug-in, within the Rhino 3dm modeling program. We acquired topography via Google earth and mapping data from GIS, brought them into Rhino 3dm, and assembled them into the base topographical surface projection of the areas being studied, which included human and natural components. This base layer became the 3d space on which functions of time and natural forces (including gravitational forces, wind forces, etc.) were then applied via Kangaroo physics. Kangaroo is a Live Physics engine for interactive simulation, optimization, and form-finding that allowed us to generate geometries that change through time, according to the physical behaviors of the material properties of the ecosystem and the human interventions within it.

In the process, we investigated strategies to increase efficiency and workability as we learned about tool limitations in terms of computing capabilities and large file sizes. Ultimately, the 3D quality of the model allows us to explore the results in different scales, views and cuts, including plan, section, axonometric, and perspective. We also have the ability to represent data with multiple graphic conventions, according to the type of data, scale, and other visualization opportunities including: color, gradient, line weight, etc.

As we continue to adapt and create more functional systems for risk reduction and restoration for sustainable coastal development we advance and refine methodologies; Our preliminary results show that it "is" possible to successfully model dynamic landscapes and that this method of visualization can allow us to more accurately project the results of human actions so that more informed decisions are made. Ultimately, our visualizations may facilitate a better understanding of human relationships to the environment's dynamic processes in a society that is eager to explore sustainability and resiliency.



Thermodynamic Insights into Surfactant Assembly in Protic Ionic Liquids

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In response to the 2010 Deepwater Horizon Oil Spill, the major strategic effort of controlling overreaching spread of crude oil was the use of dispersant. However, much is unknown of the driving forces behind the solvation process and assembly of micellar structures of said dispersants. Protic Ionic Liquids (PILs), because of their capacity to aid self-assembly of surfactants and stabilize their structures, make for choice solvents in studying these behaviors. Thus, by extensively exploring the thermodynamics of these PILs we may reveal some guiding information on surfactant behavior.

The PIL studied thus far is ethylammonium nitrate and water at varied concentrations. In order to study the behavior of these mixtures, we performed highly detailed Molecular Dynamics Simulations using GROMACS to yield density data, radial distribution functions, diffusion coefficients and other thermodynamic data. Computed results were then compared against experimental data. As a result, this study so far has in large part verified the accuracy of our computer simulated models. Further studies on the formation of aggregates, as well as studies on longer alkane chain PILs are in process.

We believe that these studies will be the foundation for future research on surfactant micellization in alkylammonium nitrates as well as directly aiding future studies on PILs.



Interfacial Activity of Oil-Degrading Bacteria and Marine Snow Formation in the Aftermath of an Oil Spill

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Purpose - The Deepwater Horizon oil spill accident in April 2010 elicited national awareness of the need to improve methods of oil spill cleanup in seawater. Interest in bioremediation has increased due to the large marine snow formation event observed in oil-contaminated surface waters of the Gulf of Mexico during the accident. The main objective of this experimental prototype study is to examine and characterize the activity of marine oil-degrading bacteria in the formation of biofilms and marine snow aggregates incorporating nonionic surfactant molecules. We investigated the development of laboratory-made artificial marine snow formed in sea water and associated biofilms at the oil-water interface. Microscopy shows uncompromised morphology of artificial marine snow and its mechanical entrapment of oil droplets. Further studies should support our hypothesis that marine snow physically and chemically alters the composition of oil droplets in various conditions. Additionally, we expect to show that marine snow formation is the result of microbial symbiosis as a biofilm at the oil-water interface.

Methods - This laboratory investigated bioremediation of crude oil in uncontaminated surface sea water collected from Lake Pontchartrain at Inner Harbor Navigation Canal. Roller table experiments modeling the Gulf of Mexico's surface water conditions were conducted in order to generate marine snow. Absorbance and Transmittance of ambient water were monitored for turbidity trends. Cryogenic Scanning Electron Microscopy (Cryo-SEM) was performed to examine the morphology and composition of marine snow. Fourier Transform Infrared (FTIR) analysis will be performed to characterize the hypothesized weathering of the oil droplets observed to be mechanically entrapped within marine snow. Uncontaminated sea water was incubated on microscope slides with crude oil to observe the formation of biofilms at the oil-water interface. Assays will be performed to distinguish microbial species and estimate microbial population sizes.

Results - Cryo-SEM imaging shows uncompromised morphology of artificial marine snow and its mechanical entrapment of oil droplets. Optical microscopy reveals microbial adsorption at the oil-water interface pertaining to the possible formation of a biofilm.

Conclusion - In summary, the imaging of the association between biofilm and marine snow formation will lead to a better understanding of the cascade of biological events encompassing bioremediation of oil spilled in sea waters.



Adhesion of Oil to Octadecyltrichlorosilane Treated Surfaces

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Oil spills affect many different parts of the environment, however few studies show the attraction of the oil to solid surfaces such as shells, rocks and sand or the effects surfactants have on this attraction. This study tests the adhesion of dodecane to surfaces (silica wafers) of different hydrophobicities, achieved by Octadecyltrichlorosilane (OTS) coating under vacuum for specific intervals of time, in pure deionized water. In later tests, Corexit (dispersant to oil ratio 1:20) will be introduced into the water and an alternative, $\sim 450\text{nm}$ carbon microspheres, which collect at the oil-water interface will be tested to see their effects on adhesion. For testing, a Tribometer with a 1 gram FUL sensor is utilized. Approximately $0.6\mu\text{L}$ of dodecane is submerged in a glass cell filled with deionized water while the silica wafers are lowered onto the droplet at $1\mu\text{m}$ per second. The force change associated with the drop attaching to the upper surface as well as detachment is recorded. It is expected that the force change will increase as the contact angle of the surface increases.



Synthesis of a Proposed Intermediate of the Molybdenum-Copper Active Site of a Carbon Monoxide Oxidation Cycle

Karry Wright, Skylar Ferrara, and Dr. James P. Donahue
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The water-gas shift reaction is a reversible reaction by which water reacts with carbon monoxide, with the aid of a catalyst, to afford carbon dioxide and hydrogen gas: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$. The water-gas shift reaction can be manipulated in either direction to produce either H_2 or CO , both of which are key industrial chemicals. Some microorganisms have carbon monoxide dehydrogenase enzymes (CODHs) that contain an active site which catalyzes reversible CO to CO_2 oxidation in an energetically efficient manner. The most common of these microorganisms are anaerobic bacteria which have a catalytic active site containing a nickel-iron-sulfur cluster. Of the two classes of CODHs, this one is the faster. Another kind of CODH occurs in an aerobic bacterium and contains a molybdenum-copper active site. This cluster is less common and catalyzes a slower reaction than the nickel-iron-sulfur cluster, but its selectivity for carbon monoxide and the little that is known about its reaction mechanism makes attractive the synthesis and study of structural analogues of its active site. **HYPOTHESIS:** Nature has selected the Mo-Cu CODH active site as optimal for running the water-gas shift reaction in air under mild conditions. By mimicking the molybdenum-copper active site of this CODH, we might obtain insight into the features that are necessary for CO to CO_2 interconversion under aerobic conditions. **METHODS:** Using a combination of new and innovative inorganic chemistry with traditional methods we can reconstruct and synthesize a molybdenum-copper complex in which metal atoms are bridged by a thiocarbonate bridge, which has been proposed to be an intermediate during the carbon monoxide oxidation cycle. These analogs are purified by recrystallization and analyzed via proton nuclear magnetic resonance spectroscopy and X-ray crystallography. **CONCLUSION:** Copper (I)-thiocarbonate complexes have been synthesized as building blocks for the further synthesis of an analogue of the Mo-(O₂CS)-Cu intermediate that has been proposed to be operative during the catalytic cycle of CODH.



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