

The Deepwater Horizon Oil Spill Response: The Connecticut Agricultural Experiment Station and the US FDA Food Emergency Response Network (FERN)



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2005: CAES Department of Analytical Chemistry Joins US FDA FERN

- One of the 8 original Food Emergency Response Network (FERN) Chemistry Cooperative Agreement Program (cCAP) Laboratories
- FERN set up through FDA (Chemistry, Radiation) and USDA FSIS (Microbiology) in recognition that agriculture and the food supply are vulnerable targets to terrorism
- For cCAP, there were 3 generation II and 3 generation III cCAPs; 14 total.
- In Sept 2010, CAES was awarded 5 additional years of funding





FERN

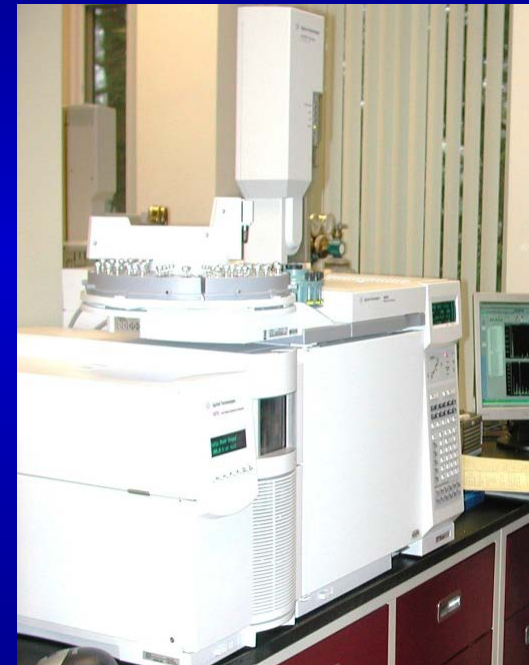
Uniting Federal, State and Local Laboratories for Food Emergency Response

Governing principle behind FERN is that cCAP Network Laboratories should have identical equipment and identical methods to run in the event of an incident.

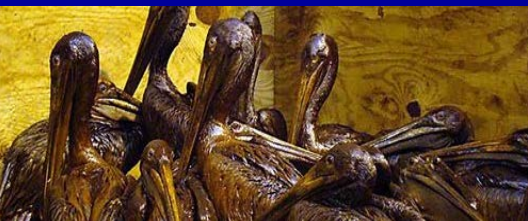


CAES Contributions to the FERN

- Instrument and method evaluations
- Participation in proficiency tests (PTs; two in 2011 so far)
- Participation in surveillance exercises; April 2011 Incident Response Drill
- FDA/FCC method extension, development, and improvement
- CAES AC staff are teaching FDA-run courses on GC/MS for FERN
- CAES has hosted FDA technical meetings/training sessions
- June 2010- Oil, Oil, and more Oil



Deepwater Horizon Oil Spill- April 20, 2010



FERN
Uniting Federal, State and Local Laboratories for Food Emergency Response

Deepwater Horizon: By the numbers

- Initial explosion occurred at 10:45am EST on April 20, 2010
- 11 workers died; the rig burned for nearly 2 days and sank on morning of April 22. First oil slick sighted that afternoon.
- Lots of early effort on determining rate of leak; had little to do with stopping the flow.
- Early estimates by BP/Coast Guard were 1000 barrels/day; outside scientists estimated up to 100,000 (turns out to be the worst case scenario value on the BP permit). One barrel holds 42 gallons of oil.
 - Final estimate was 53,000 barrels per day
 - Interesting note- Fines are often based on amount of oil leaked
- By April 30, spill covered 3,850 square miles of the Gulf were covered with the slick



Deepwater Horizon: By the numbers

- Efforts to stop the leak were complicated by numerous factors, including the fact that the well-head was over 5000 ft below the surface
- By July 30, 2010 over 1.8 million gallons of dispersant (mostly Corexit 9500) had been used at the surface
- An additional 1.1 million of gallons of dispersant was used at the wellhead
- Dr. Brian Eitzer and Dr. Christina Robb (CAES) worked with FDA in developing detection methods in seafood
- There has been a lot of debate over the toxicity of these chemicals; what I know for sure:
 - Dispersants are less toxic than most constituents of oil
 - Dispersants have never before been used at this magnitude or under these conditions



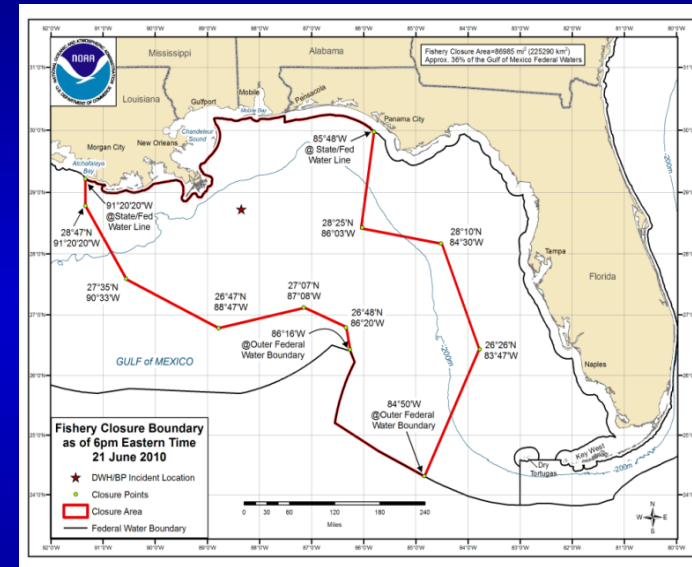
Deepwater Horizon: By the numbers

- The well was capped on July 15 and “killed” on September 19
- Approximately 205,800,000 gallons of crude oil were released from the well; the 5th largest spill on record. And the survey says...
 - 17% recovered directly from the well
 - 5% burned at the surface
 - 3% skimmed from the surface
 - 8% chemical dispersed
 - 16% naturally dispersed
 - 25% evaporated or dissolved
 - **26% REMAINING**
- 26% is 54 million gallons; more than twice Exxon Valdez
- Some say dispersed and dissolved are toxicologically relevant; raises that residual value to 52-67% or 107-140 million gallons



Re-opening Protocols for Closed Commercial Fisheries

- Almost immediately, large areas of state and federal waters were closed to commercial fishing (approx. 88,000 square miles)
- Re-opening protocols for closed federal (NOAA) and state waters established (FDA) by mid-May.
- Original re-opening protocol is set up with tiered testing consisting of 3 levels
- First, states can only collect seafood samples from closed waters that are visibly oil free.
- Seafood samples include shrimp, oysters, crab, finfish (well over a dozen species)
- Second, these samples would be delivered to a NOAA Laboratory in Pascagoula MS for organoleptic or sensory analysis



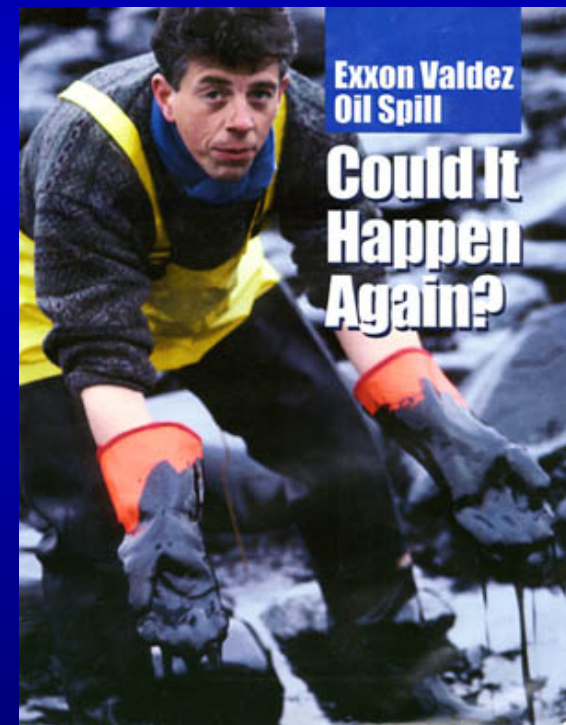
Level 2- NOAA/FDA Organoleptic Analysis

- Three separate levels of organoleptic analysis are conducted by NOAA/FDA experts at the Mississippi lab.
- These are indeed highly trained experts in sensory analysis. Initial press reports indicated possible training of unemployed fisherman...a nice story but smells kind of fishy...
- NOAA/FDA Sensory Panels are two 8-member teams; can detect oil taint in seafood to around 5ppm.
- Sensory/olfactory analysis occurs on initially on raw samples, then on cooked samples. Finally, samples are tasted.



Original Level 3- “The NOAA Method”

- If 5 of 8 panel members pass a sample, it was then to go to chemical analysis by the “The NOAA Method.”
- The NOAA method is a rigorous and definitive GC/MS analysis for PAHs and oil-related contaminants in seafood
- Developed after Valdez in Alaska (1989) and survived scrutiny in a court of law; the significance of this point cannot be underestimated
- However,...



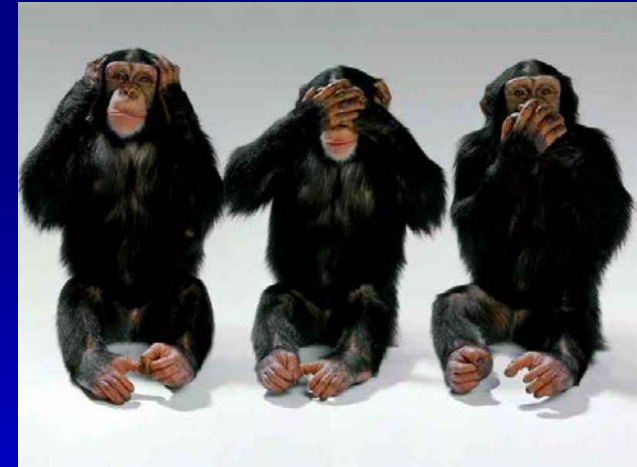
“Houston; we’ve got a problem...”

- The NOAA method is described in a 64-page document and involves accelerated solvent extraction (ACE) with dichloromethane, followed by clean-up by silica/alumina columns and size exclusion HPLC. Analysis is by GC-MS.
- May 27, 2010- Of all NOAA, FDA, and cCAP FERN State Labs, only three had the necessary equipment on hand for the NOAA method (one had most of it in closet). Cost to get the equipment was about \$100,000/lab; minimum 2-3 months to receive, install, and validate equipment/method.
- In addition, the NOAA method has very low throughput; 17 samples per week per lab.
- At the same time, the NOAA Administrator predicts maximum of 90,000 samples may be needed to re-open all closed waters



And Then Things Got Political...

- Governors of some Gulf Coast States were holding daily press conferences accusing NOAA/FDA of dragging their feet on testing.
- One Gulf Coast Governor had the National Guard collect a “truck-load” of seafood and delivered it to the NOAA/FDA MS laboratory. No paperwork on location, species or time of collection.
- Gulf Coast Senators (of both political parties) had a conference call with FDA Administrator Margaret Hamburg; I’ve been told that it was very far from pleasant...
- It would be an understatement to say that there was tremendous interest in re-opening closed waters when no contamination was found; having a back-log of untested seafood due to NOAA method shortcomings was not an option.
- A decision was made in early June that the re-opening protocol needed to be modified quickly so that when the oil flow was stopped; testing could begin immediately.



Washington, we've got a solution

- On June 9th 2010, officials from FDA Headquarters visit the Forensic Chemistry Center (FCC); the technical lead in the FERN cCAP Program
- FCC is told to IMMEDIATELY develop a new chemical screening test that could be implemented after samples pass organoleptic analysis but before NOAA analysis.
- That same day, I received an ominous message from FCC requesting an immediate conference call; MN Department of Agriculture was also contacted.
- On that call, we decided to develop a QuEChERS-based (Quick, Easy, Cheap, Effective, Rugged, Safe) extraction of seafood followed by an HPLC-FLD screening procedure to estimate 15 PAHs and total oil contamination. The original plan also called for development of a modified GC-MS method for confirmatory analysis. However, the was tabled/dropped due to external pressure and the need to quickly stand up the new screening method.
- HPLC-FLD advantages- The equipment is more widely available; throughput of 100 samples per week per lab.



Washington, we've got a solution

- Levels of concern for 15 PAHs (7 carcinogens) established by FDA CFSAN for four matrices (crab, shrimp, oyster, finfish)
- Method development begins immediately; three conference calls per week and many, many emails. The primary goal was to have a chemical screening test that was as simple and as accurate as possible so as to be deployed on a large scale if necessary.
- Decisions had to be made on many aspects of the method: Tissue/solvent amounts? Water addition? Mixing conditions (time, rigor)? Extract clean-up by PSA/C18? Spiking levels? Calibration levels? Instrument conditions? Alkyl homologues? SRM1974b- PAHs in mussel tissue?



Washington, we've got a solution

- Finalize the extraction and analysis conditions by July 19th 2010.
- Method validation begins on Monday July 19th (4-days after well capped); spiking of PAHs into clean seafood matrices.
 - Matrices purchased locally; live crab purchased.
 - How many chemists does it take to shuck an oyster...fewer than it takes to get meat from a crab...
 - 15 PAHs spiked into each matrix at 3 levels (0.025, 1, 10 ppm). Percent recovery, MDL, LOQ, other QA/QC items calculated for each analyte in each matrix.



Washington, we've got a solution

- CT validation completed by Wednesday July 21st 2010
- On Wednesday July 21, FCC calls and says that the method will be presented to FDA CFSAN, FDA DFS, and CDC for approval on Monday July 26th in Cincinnati Ohio (at FCC).
- On Thursday July 22nd, FCC calls and says the FDA Commissioner moved the meeting to Saturday morning July 24th.
- CT and MN fly to Ohio. Meeting starts at 9am; by 4pm, the method is approved. CT and MN fly home in shellshock (I was told to expect up to 20 samples per day, 6 days a week, for up to 6 months...)
- Method posted on the FDA website Monday July 26th.
- CAES gets first seafood on Wednesday July 28th and received shipments up until October 28, 2010.



SCREEN FOR THE PRESENCE OF POLYCYCLIC AROMATIC HYDROCARBONS IN SELECT SEAFOODS USING LC-FLUORESCENCE

Samuel Gratz¹, Angela Mohrhaus¹, Bryan Gamble¹, Jill Gracie¹, David Jackson¹, John Roetting¹, Laura Ciolino¹, Heather McCauley², Gerry Schneider², David Crockett², Walter Kruel², Terri Arsenault², Jason White², Michele Flotzmaier², Yoko Johnson², Douglas Heiklinger², Fred Fricks²

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Abstract

A liquid chromatography with fluorescence detection (LC-FLD) method has been developed to screen for fifteen targeted polycyclic aromatic hydrocarbons (PAHs) at concentrations below the established levels of concern in oysters, shrimp, crabs and fanfish. The procedure was validated by spike recovery experiments at three levels for each matrix, and through analysis of NIST standard reference material SRM 1974b. PAHs are extracted using a modification of the quick, easy, cheap, effective, rugged and safe (QuEChERS) sample preparation procedure, employing acetonitrile (ACN) as the solvent. The extracts are filtered using 0.2 micron syringe filters, but require no post-extraction sample cleanup for LC-FLD analysis. The chromatographic method employs a polymeric C18 stationary phase designed for PAH analysis by gradient elution to separate fifteen targeted PAHs in a 35 minute run time. For the analysis of unknowns, a sample that is determined to be positive for a targeted PAH at or above 50% of the FDA level of concern requires that confirmatory analysis be performed. Additionally, an estimate of total PAH concentration including alkyl homologues in the sample is calculated. Samples containing total PAH concentrations greater than 50% of the FDA level of concern for asphaltene require that confirmatory analysis be performed.

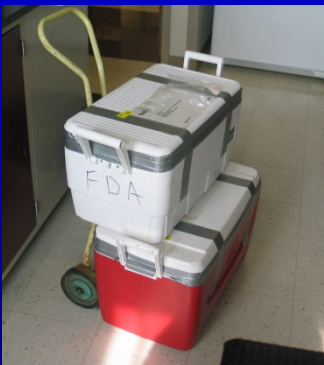
CAES Seafood Testing Program

- Samples shipped with less than 24 hour notice; results reported to FDA via secure website within 24 hours of sample receipt.
- Initial concerns over sample condition upon receipt (crates of crabs...)
- Initially, FDA CFSAN, FDA DFS, and the Whitehouse were reviewing our data. Re-opening decisions made within 2-3 hours. And by data, I don't just mean the numbers. Full data packages had to be produced (chromatograms, standards, excel sheets with calculations,...)



CAES Seafood Testing Program

- As of mid November, CAES, MN, and FCC were the only labs running the new screening method
- 18 labs were in the process of coming on line
- 8 labs came on line for NOAA method; 4 cCAP and 4 FDA (Federal waters, parallel testing program)
- Of the 2400 seafood samples tested, none failed. For the LC-FLD screen, failure was:
 - If one of the 15 PAHs was present at 50% of its level of concern (would have gone to NOAA method for confirmation) OR
 - If the total estimated PAH content (AUC from 2.5-20 min) was 50% of FDA LOC for naphthalene in that matrix (16-62 mg/kg)



CAES Seafood Testing Program

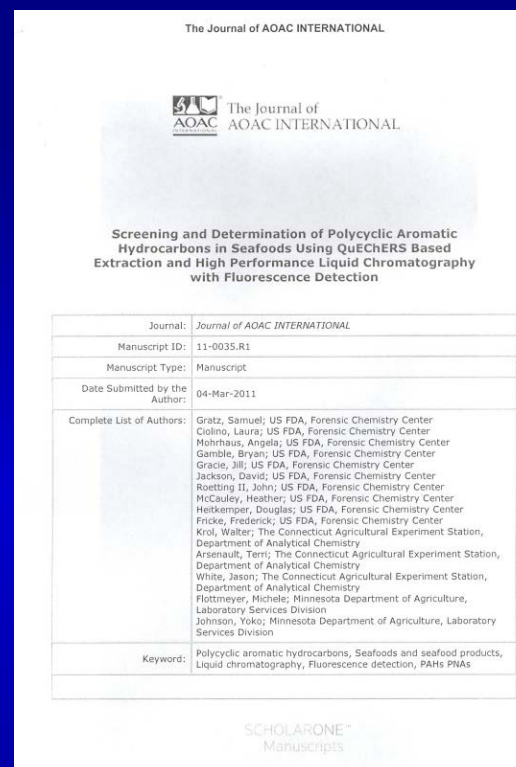
- CAES issued two press releases; 14 interviews (radio, television, newspaper) in 10 days.

DEEPWATER HORIZON OIL SPILL RE-OPENING SAMPLES: PAH RESULTS SUMMARY FROM FDA PAH TESTING LABS								PAH ANALYTES (LEVELS OF CONCERN [LOC] AND COMPOUNDS OF INTEREST FROM RE-OPENING PROTOCOL, JULY 26th 2010 VERSION) For each sample total fractional amount reported is the sum of levels detected for each carcinogenic analyte (indicated with a star) as a percentage of the permissible level applicable to that analyte. TR = Trace (<< ppm) LOD= limit of detection na = Not Applicable (analyte not analyzed for)														NPH=Naphthalene, FLU=Fluorene, PHN=Phenanthrene; ANT=Anthracene, FLA=Fluoranthene, PYR=Pyrene, BaA=Benzo(a)anthracene, CHR=Chrysene, BbF=Benzo(b)fluoranthene, BkF=Benzo(k)fluoranthene, BaP=Benzo(a)pyrene; DBaA=Dibenz(a,h)anthracene; IcdPy=Indeno(1,2,3-cd)pyrene						
RESULTS REPORTED USING: Screen for the Presences of Polycyclic Aromatic Hydrocarbons in Select Seafoods Using LC-Fluorescence								LOC Shrimp & Crabs (ppm)	123	246	1846	246	185	1.32	132	1.32	13.2	0.132	0.132	1.32	61.5	** This represents a very conservative, "worst case" estimate of the total amount of PAHs including alkyl homologs in the sample and may include many unidentified compounds other than PAHs. *** If the estimated total PAHs exceeds 50% of the level of concern for naphthalene, then the sample will be sent for confirmatory analysis using the NOAA PAH method.						
Sensory Results	Comp ID by Reopening Area (State-Area_Site)	State Identifier	State Origin	Lab Recvd Date	Lab DOC	Matrix	Comments	NPH (ppb)	FLU (ppb)	PHN (ppb)	ANT (ppb)	FLA (ppb)	PYR (ppb)	*BaA (ppb)	*CHR (ppb)	*BbF (ppb)	*BkF (ppb)	*BaP (ppb)	*DBaA (ppb)	*IcdPy (ppb)	**Est Tot PAH (ppm)	Total Fractional Amount (This is a sum of all percentages for carcinogenic analytes indicated with a star and should be less than 1 for the sample not to be violative)	***Exceed 50% NPH's LOC?					
Pass	FLPnsdAclsure_FWRI	SMP1002159	FL	7/29/2010	7/30/2010	fish																						
Pass		SMP1002159		7/29/2010		fish																						
Pass		SMP1002159		7/29/2010		fish																						
Pass		SMP1002159		7/29/2010		fish				TR	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0	no
Pass		SMP1002159		7/29/2010		fish																						
Pass		SMP1002159		7/29/2010		fish																						
Pass	FLPnsdAclsure_FWCLE_A	GMD 2010070115	FL	7/29/2010	7/30/2010	fish																						
Pass		GMD 2010070115		7/29/2010		fish																						
Pass		GMD 2010070115		7/29/2010		fish																						
Pass		GMD 2010070115		7/29/2010		fish																						
Pass		GMD 2010070115		7/29/2010		fish																						
Pass		GMD 2010070115		7/29/2010		fish				TR	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0
Pass	FLPnsdAclsure_FWCLE_B	GMD 2010070115	FL	7/29/2010	7/30/2010	fish																						
Pass		GMD 2010070115		7/29/2010		fish																						
Pass		GMD 2010070115		7/29/2010		fish																						
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Pass		GMD 2010070115		7/29/2010		fish																						
Pass	FLPnsdAclsure_Unkwn_A	SMP1002157	FL	7/29/2010	7/30/2010	fish																						
Pass		SMP1002157		7/29/2010		fish																						
Pass	FLPnsdAclsure_Unkwn_B	SMP1002161	FL	7/29/2010	7/30/2010	Shrimp																						
Pass		SMP1002161		7/29/2010		Shrimp																						
Pass	FLPnsdAclsure_Unkwn_C	SMP1002161	FL	7/29/2010	7/30/2010	Shrimp																						
Pass		SMP1002161		7/29/2010		Shrimp																						
Pass	FLPnsdAclsure_Unkwn_D	SMP1002161	FL	7/29/2010	7/30/2010	Shrimp																						
Pass		SMP1002161		7/29/2010		Shrimp																						
Pass	FLPnsdAclsure_Unkwn_E	SMP1002160	FL	7/29/2010	7/30/2010	fish																						
Pass		SMP1002160		7/29/2010		fish																						
Pass	FLPnsdAclsure_Unkwn_F	GMD 1007011801	FL	7/29/2010	7/30/2010	fish																						
Pass		GMD 1007011801		7/29/2010		fish																						
Pass		GMD 1007011801		7/29/2010		fish																						



Current Status- April 2011

- The new HPLC-FLD screening method has been accepted for publication in the *J.AOAC International* (peer reviewed journal).
- Effective November 30, 2010 the FERN cCAP was deactivated.
- Letter of appreciation sent from FDA to CT Governor (Jan.2011).
- 97% of state fisheries had been re-opened; a small section LA fisheries remain closed until late Spring 2011.
- FDA is planning a 2-year surveillance program. Sampling occur at processing plants and use FDA labs for FERN cCAP labs will provide surge capacity.
- Of the 88,522 square miles originally closed (37% of the Gulf), roughly 1,100 square miles was still closed as of mid-Nov.
- On November 24, 4,200 additional square miles were closed after a shrimper pulled up tar-balls with his catch of royal red shrimp (collected from a depth of 600 feet).
- BP had pledged \$450 million in competitive oil spill research funding; was to be released in January 2011 but no sign of the funds yet. EPA has released a RFP worth \$2.5 million.





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