

Pesticide Analysis in the Wake of Katrina and Rita : Analytical Lessons Learned

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Who We Are

- Joint venture
 - Louisiana State University Agricultural Center
 - Louisiana Department of Agriculture & Forestry
- Located on the LSU Campus - Baton Rouge

What We Do

- Analyses for Researchers within the LSU Agricultural Center
- Analyses as Regulatory Laboratory for Louisiana Department of Agriculture & Forestry
- Analyses for Researchers within the LSU A&M System
- Analyses for the Public

What Happened

- Hurricane Katrina 8/29/05
- Hurricane Rita 9/24/05
- Coastline is inundated by storm surge and levee breaches
- Our lab in Baton Rouge doesn't even lose power during Katrina!





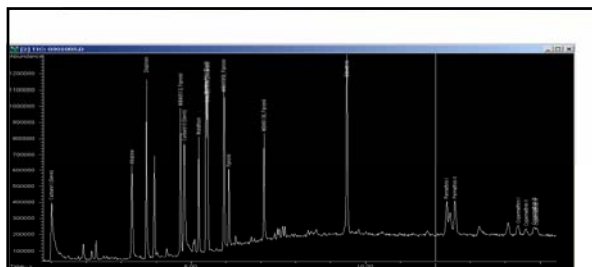
- ### Offering Our Services
- EPA Region 6
 - Houston Lab sends mobile unit with GC/MS
 - We offer assistance and volunteer parts
 - Louisiana Department of Environmental Quality (LDEQ)
 - Requests Pesticide Analysis of Katrina waters
 - We suggest list of analytes to target and agreement is reached in one face to face meeting!

- ### Defining the Assignment
- List of Targeted Pesticides created based on the mainly urban nature of flooded area in Katrina
 - Agreed that any major peaks would also be investigated
 - Addition of PCBs added to target list when requested by LDEQ – (MDL @ 7.00ppb)
 - Results will be transmitted electronically as much as possible between labs

- ### Staff's Microbiological Concerns
- We don't want to touch "TOXIC SOUP"
 - Call in the Campus Experts
 - Following the Recommendations
 - Disinfection before delivery
 - Biohazard labeled carts
 - Wipe downs of work areas
 - Bleach treatment before disposal

Targets and MDLs

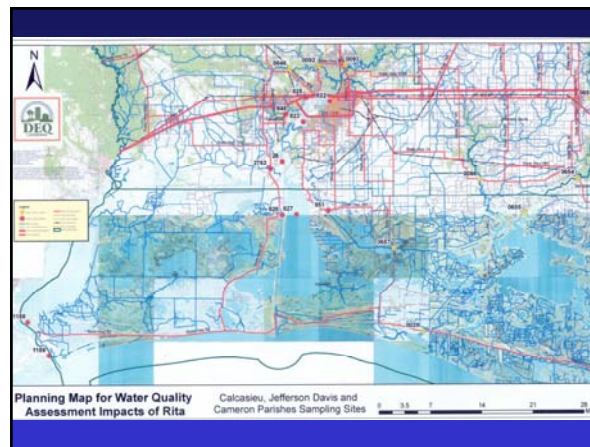
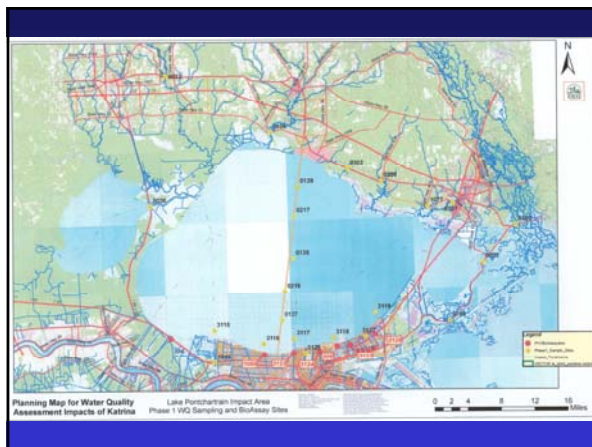
• PCBs	7.00ppb
• Termiticides	
– Fipronil & Metabolites	0.20ppb
– Cypermethrin	0.50ppb
– Bifenthrin	0.20ppb
– Permethrin	0.50ppb
– Chlorpyrifos	0.20ppb
– Imidacloprid	1.00ppb
• Household Use	
– Malathion	0.20ppb
– Diazinon	0.20ppb
• Garden Use	
– Atrazine	0.20ppb
– Metolachlor	0.50ppb
– Carbaryl (Sevin) NPD	5.00ppb



GC Standard Mix –Scan Mode
 Sevin @ 1ppb Others @ 0.40ppb (on column)
 (PCBs not included in this mix)

Sample Sites

- LDEQ responsible for Sites and Sample Collection
- Katrina Sites -- 59
- Rita Sites -- 52
- 338 –Number of Samples Analyzed
- Received 09/12/05 thru 11/16/05



Extraction Procedure

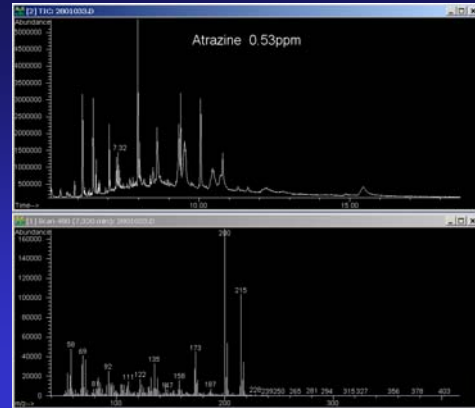
- Liquid/Liquid Extraction
 - 3 X 75ml Methylene Chloride Partition
- Based on EPA Methods 507/508
- 500ml Sample Size
- Final Solvent – Hexane
- Split final extract between GC and HPLC analysis
- Solvent exchange to Acetonitrile for HPLC analyses of Imidacloprid
- Concentrated to 500ml/ml before analysis
- **Initial samples analyzed at 2mls due to unknown matrix interferences

HPLC Analysis for Imidacloprid

- Agreement to analyze for Imidacloprid for only the Initial sampling of each Site – unless positives are found
- Waters 2690 with Dual UV Detector
- Wavelength: 270nm
- Columns (change column for confirmation)
 - ODS2 – 4.6 x 250mm 5micron
 - SB Phenyl – 4.6 x 250mm 5 micron
- Mobile Phase: 60%Acetonitrile / 40%Water
- Flow 1.25ml/min

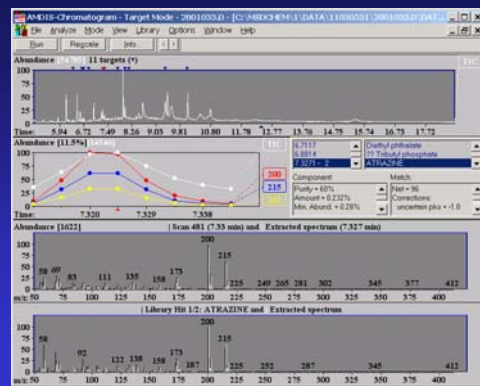
GC Analysis Plan A

- Initial screen on HP5890 with ECD/NPD
- Suspected positives confirmed and quantitated on second instrument Agilent6890s with dual ECD or dual NPD
- All positives confirmed by GC/MS
- TOO MANY PEAKS FOR ANALYSIS TIME ALLOWED
- NEED A PLAN B!



Embracing a New Tool

- AMDIS – Automated Mass Spectral Deconvolution and Identification Software
- Analyzes background noise, detects components and calculates a “clean” spectra by subtraction then searches library to identify
- Developed at NIST with support from DOD
- FREE on Internet–
<http://chemdata.nist.gov/mass-spc/amdis>
<http://www.amdis.net>

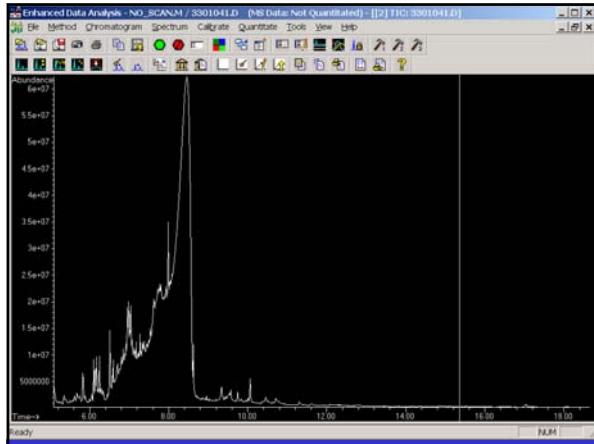


GC Analysis Plan B

- USE OUR NEW TOOL! AMDIS
- Scan sample on HP5973 GC/MSD
- Run through AMDIS Deconvolution
- Run on HP5890 ECD/NPD for PCB screen
 - for old time's sake! - it's a “comfort” issue
- Positives on ECD/ECD or NPD/NPD
 - External point quantitation

Interferences and Asides

- Mysterious vanishing layers
 - Initial Katrina samples only
 - Decided to analyze at 250ml/ml “just in case”
- DEET (N,N-diethyl-meta toluamide) Abundant
 - Useful tracer of “re-used” water (USGS)
 - Nationwide surface water study found in 74% of samples
 - LDAF Surface Water findings at a similar rate
 - Inform LDEQ since it is outside our analysis targets
 - First became aware of presence by AMDIS



Interferences Cont.

- Sulfur 8?
 - Large interference peaks on ECD and MS
 - MS Library search and AMDIS list - Sulfur (8)
 - Mainly same sites on Pontchartrain
 - Theories of source abound!
 - Natural gas leaks?
 - Runoff from Sulfur producing plant?
 - Other morbid suggestions
 - Inform LDEQ since it is outside our analysis targets

Results-Very Few Positives

- Targeted Pesticides Found
 - Atrazine
 - Seven Sites @ < 0.35ppb
 - One Site 0979 10/25 0.53ppb
 - Malathion Site 1159 10/18 0.40ppb
 - Imidacloprid Site 0003 10/27 1.44ppb
- Other Pesticides Found
 - Bromacil & Hexazinone at Single Site – 0825
 - 10/18 –2.12ppb & 0.23ppb
 - 11/01- 1.56ppb & 0.25ppb

LDEQ-Other Parameters

- Analyses by LDEQ Labs, Contract Labs, LDHH, USGS
 - Conventional Parameters
 - TrueColor, Specific Conductance, TDS, TSS, Chloride, Sulfate, Alkalinity, Turbidity, Hardness, Ammonia Nitrogen, TKN, Nitrate+Nitrite N, TP TOC
 - Fecal Coliforms
 - Metals
 - Na, Cu, Ni, Pb, Zn, Cr, Cd, As, Hg
 - Al, Ba, Be, Ca, Co, Fe, K, Mg, Mn, At, Se, Si, Ti, Va (groundwater)
 - Organics (Volatiles (some in Air), Semivolatiles)
 - Other Analysis
 - COD, BOD, Cyanide (Phase I only)
 - Phenol, Hexavalent Cr, Oil & Grease, Bioassays,
 - Soils – Gamma Radiation/NORM, TPHs, PAHs

Quarantine on Wood Products

- Formosan Termite Infestation Must Be Contained
- LDAF Commissioner Bob Odom issued Quarantines following Katrina and Rita on all Wood Products in Affected Areas
 - Fallen tree material
 - Salvaged materials from homes (beams, doors)
 - Rumors regarding Infested Mulch circulate
 - Hits on AgCenter website increase dramatically
- Bracing for Analyses to Come
 - Structural Applications to Enforce in Formulations
 - Wood Mulch to Investigate

Rita's Salt Intrusion

- Storm Surge -- Rice fields most affected
 - Tolerance ~ 1300ppm
- AgCenter Extension Service and Soil Testing Lab (STPAL)
 - Collected over 500 samples from 177 sites
 - Some areas as high as 20,000ppm
- LDEQ provided results on floodwaters in area
- LDAF submitted sugarcane field soils tested by our Lab
 - Results ranged 1170 – 7100ppm
- Remediation
 - Rainfall to wash – experiencing drought
 - Gypsum addition to soil – expensive
 - Recommending converting to pasture for this year
- GOOD NEWS
 - Killed Peruvian Water Grass—Invasive Weed
 - Salt Levels have dropped 60% in some areas

Watermelons

- Watermelons sprout spontaneously in St. Bernard Parish after waters recede!
- Normally planted in April –These ripe in Dec
- Public wants to know if they are “toxic”
- Biologist Dr. Gary Ross submits fruit and soil samples for pesticide scan and metals
- Pesticide Findings-
 - Watermelon negative
 - Soils have low levels of structural pesticides
 - HCB 0.02ppm Permethrin 0.08ppm Fipronil 0.02ppm
- Hurry Up! The National News media keeps calling me!

Other “Impacts”

- Housing “Evacuee” Researchers
- Walking the Dogs
- LDAF Employees helping around the State
- AgCenter distributes Mold Clean-up and Storm Prep Literature
- LDAF 10% paycut
- AgCenter Exigency Approved
- AgCenter Suffers Physical Damage
 - 4 extension offices lost
 - 18 of 20 research stations suffered
- FEMA Bandwagon
- Nagin Commercials in Baton Rouge!

Continuing Relationships

- Established relationship with LDEQ continues
- Samples for other pesticide “incidents” readily requested and accepted
- Tours of respective facilities and shared information improve our operations
- Experience removed the “Fear Factor”

Final Thoughts

- AMDIS is Amazing – Don’t leave home without it!
- State Agencies can learn to work together and trust each other- even in Louisiana!
- Fulfilling our role as public servants is very gratifying – especially in times of crisis



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