





**Catfish Pesticide Residue Testing for
USDA-PDP and USDA-FSIS-Catfish
Inspection Program**

**Florida Pesticide Residue Workshop
July 21, 2010
Jonathan Barber**





PDP Catfish Sampling

- Catfish samples collected by USDA-PDP state inspectors
 - April 1, 2008 – March 30, 2009 for USDA-PDP
 - July 1, 2009 – June 30, 2010 for USDA-FSIS
- 62 samples per month, or a total of 1488 samples, were targeted for collection
- Samples included domestic and imported samples, including farm-raised catfish



PDP Catfish Sampling

- Samples were collected under PDP's sampling frame (a statistically-based system that yields nationally representative samples of what is available to the consumer)
- Samples are collected by PDP samplers at distribution centers and terminal markets, including wholesale or fish markets



PDP Catfish Sampling

- Eligible samples included anything labeled as "catfish"
- Acceptable samples included fresh or frozen raw catfish (cleaned and skinned)
- Acceptable sample types included boneless forms such as fillets, nuggets, strips, or steaks as well as cleaned and skinned with bones



PDP Catfish Sampling

- Each sample consisted of 1 – 3 pounds and shipped to the USDA-AMS-NSL laboratory for pesticide residue testing
- Beginning in July 2009, 2 pounds were also shipped to USDA-FSIS for other additional testing



Sample Preparation

- Samples are cut into small chunks and homogenized in dry ice using a Robo-Coupe.
- Samples are allowed to sublime overnight in -20 °C freezer .
- Long term storage in -70 °C freezer.









Pesticide residue extraction methodology

- 20 gram subsample is extracted with ethyl acetate
- Solvent exchanged to acetonitrile
- Fat is removed using freezing and 1 gram C18 column SPE clean-up while the sample is in acetonitrile
- LC/MS/MS fraction further cleaned up using dispersive SPE using PSA
- GC/MS-EI and NCI fraction further cleaned up utilizing column SPE using PSA and solvent exchanged to toluene



Pesticide residue extraction methodology

- Sample concentration is 4 grams/mL
- Column SPE clean up performed using positive pressure manifold
- Separate C18 column clean-up procedure is more effective at removing fat



Instrumental Analysis

- 220 Total Compounds Analyzed in Catfish
- GC/MS-EI – 74 analytes
- GC/MS-NCI – 85 analytes
- LC/MS/MS – 61 analytes
- Internal Standards utilized
- Matched Matrix Calibration Standards



Detection & Recovery Data: 2008-09 USDA-PDP

Analyte name	Detections 744 samples	Low (ppb)	High (ppb)	LOQ (ppb)	Avg. % Rec.	Detection Method
Atrazine	5	2.0	4.8	2	106	LC/MS/MS
BHC beta	5	1.2	35.3	1	96	GC/MS-NCI
Bifenthrin	17	1.0	5.0	1	102	GC/MS-NCI
Chlordane, cis isomer	7	1.1	2.1	1	89	GC/MS-NCI
Chlordane, trans isomer	1	1.0	1.0	1	100	GC/MS-NCI
Chlorpyrifos	41	1.0	5.1	1	105	GC/MS-NCI
Chlorpyrifos methyl	13	1.0	2.9	1	109	GC/MS-NCI
Cyhalothrin [sum]	7	1.1	3.4	1	98	GC/MS-NCI
Cypermethrin [sum]	20	1.0	5.3	1	88	GC/MS-NCI
DCPA (Chlorthal)	1	3.6	3.6	1	109	GC/MS-NCI
DDD o,p'	120	1.0	6.4	1	106	GC/MS-EI
DDD p,p'	315	1.0	138	1	119	GC/MS-EI
DDE o,p'	34	1.0	9.6	1	102	GC/MS-EI
DDE p,p'	608	1.0	580	1	95	GC/MS-EI
DDT p,p'	13	1.2	15.1	1	82	GC/MS-EI

Detection & Recovery Data: 2008-09 USDA-PDP

Analyte name	Detections 744 samples	Low (ppb)	High (ppb)	LOQ (ppb)	Avg. % Rec.	Detection Method
DEF (Tribufos)	13	1.0	6.7	1	99	GC/MS-NCI
Diclofop methyl	1	1.1	1.1	1	109	GC/MS-EI
Dicofol p,p'	23	1.0	23.3	1	112	GC/MS-NCI
Dieldrin	8	7.4	15.5	5	99	GC/MS-NCI
Diflubenzuron	3	2,600	11,600	13	115	LC/MS/MS
Diphenylamine (DPA)	140	1.0	47.0	1	126	GC/MS-EI
Diuron	58	16.6	178	16	106	LC/MS/MS
Endosulfan I	12	1.0	6.2	1	90	GC/MS-NCI
Endosulfan II	2	1.5	3.5	1	108	GC/MS-NCI
Endosulfan sulfate	46	1.0	23.0	1	105	GC/MS-NCI
Esfenvalerate+Fenvalerate	1	1.0	1.0	1	98	GC/MS-NCI
Famoxadone	3	10.2	11.8	10	103	GC/MS-EI
Hexachlorobenzene (HCB)	4	1.0	5.1	1	61	GC/MS-NCI
Lindane (BHC gamma)	3	2.1	3.1	2	96	GC/MS-NCI
Metolachlor	1	4.4	4.4	2	108	GC/MS-EI

Detection & Recovery Data: 2008-09 USDA-PDP

Analyte name	Detections 744 samples	Low (ppb)	High (ppb)	LOQ (ppb)	Avg. % Rec.	Detection Method
MGK-264	3	9.0	27.8	5	109	GC/MS-EI
Nonachlor, cis isomer	6	1.4	2.3	1	101	GC/MS-NCI
Nonachlor, trans isomer	8	1.0	4.6	1	96	GC/MS-NCI
Oxadiazon	3	2.4	6.5	2	96	GC/MS-NCI
Pendimethalin	29	2.0	18.1	2	106	GC/MS-NCI
Pentachloroaniline (PCA)	29	1.0	24.3	1	88	GC/MS-NCI
Piperonyl Butoxide	2	2.1	4.3	2	110	GC/MS-EI
Pirimiphos methyl	8	1.4	22.9	1	108	GC/MS-EI
Propetamphos	1	1.4	1.4	1	104	GC/MS-EI
Quinoxifen	1	21.9	21.9	3	94	GC/MS-EI
Terbutryn	1	25.8	25.8	1	105	GC/MS-EI
Tetraconazole	1	2.0	2.0	2	112	GC/MS-NCI
Thiabendazole	1	3.1	3.1	2	58	LC/MS/MS
Toxaphene [sum]	66	50.0	449	50	101	GC/MS-NCI

Detection & Recovery Data: 7/09 - 4/10 USDA-FSIS

Analyte name	Detections 601 samples	Low (ppb)	High (ppb)	LOQ (ppb)	Avg. % Rec.	Detection Method
Acetochlor	2	7.7	8.8	6	109	GC/MS-EI
Atrazine	4	2.5	17.9	2	104	LC/MS/MS
BHC alpha	12	1	8.1	1	94	GC/MS-NCI
BHC beta	2	4.8	7.2	5	91	GC/MS-NCI
BHC delta	5	3	6.6	1	98	GC/MS-NCI
Bifenthrin	162	1	60	1	111	GC/MS-NCI
Chlordane, cis isomer	2	1.3	1.4	1	99	GC/MS-NCI
Chlordane, trans isomer	1	1.2	1.2	1	103	GC/MS-NCI
Chlorpyrifos	51	1	40	1	133	GC/MS-NCI
Chlorpyrifos methyl	11	1	2.9	1	99	GC/MS-NCI
Cyhalothrin [sum]	4	1	7.8	1	123	GC/MS-NCI
Cypermethrin [sum]	10	1.2	11.1	1	119	GC/MS-NCI
Cyphenothrin	1	102	102		116	GC/MS-EI
DDD o,p	19	2.2	60.8	1	78	GC/MS-EI
DDD p,p	151	2	133	1	123	GC/MS-EI
DDE o,p	8	2.3	11.9	1	95	GC/MS-EI

Detection & Recovery Data: 7/09 - 4/10 USDA-FSIS

Analyte name	Detections 601 samples	Low (ppb)	High (ppb)	LOQ (ppb)	Avg. % Rec.	Detection Method
DDE p,p	367	2	2310	1	119	GC/MS-EI
DDT p,p	2	2.5	10.2	1	80	GC/MS-EI
Deltamethrin [sum]	1	11.8	11.8	10	114	GC/MS-NCI
Dicofol	2	1.4	3.1	1	106	GC/MS-NCI
Dieldrin	6	5.7	29.2	5	114	GC/MS-NCI
Diphenylamine (DPA)	3	2.1	3.6	2	80	GC/MS-EI
Diuron	35	16.1	179	16	101	LC/MS/MS
Endosulfan I	5	1.1	2.6	1	107	GC/MS-NCI
Endosulfan II	2	1.1	3.8	1	108	GC/MS-NCI
Endosulfan sulfate	39	1	28.4	1	138	GC/MS-NCI
Esfenvalerate [sum]	10	1	8.9	1	126	GC/MS-NCI
Hexachlorobenzene	2	1.5	1.8	1	79	GC/MS-NCI
Lindane	5	2.2	3.7	2	96	GC/MS-NCI
MGK-264 total	1	16	16	16	110	GC/MS-EI

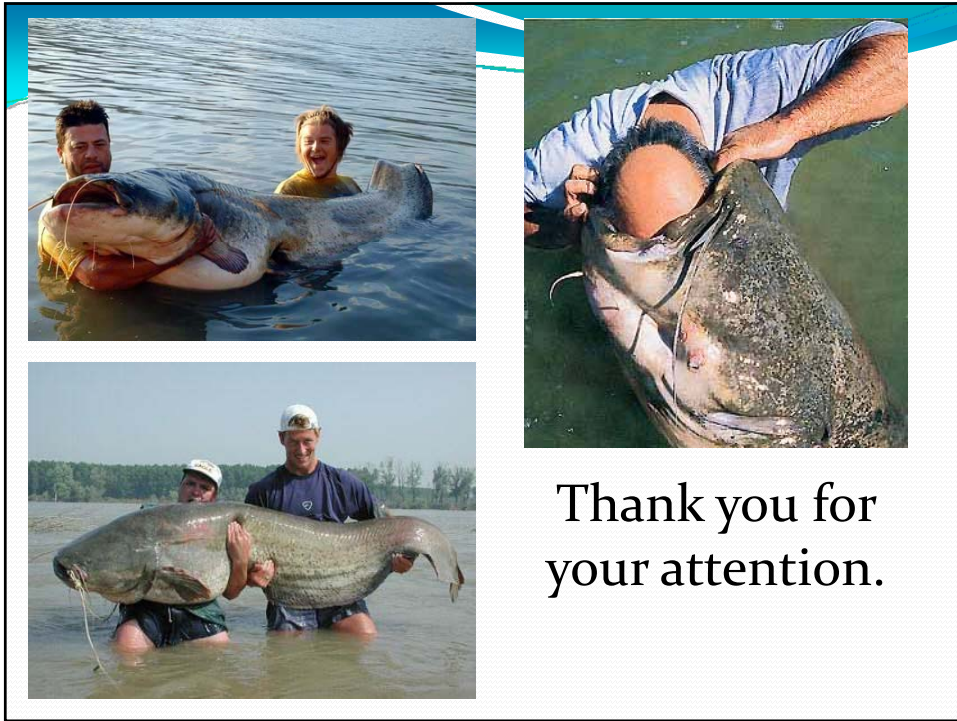
Detection & Recovery Data: 7/09 - 4/10 USDA-FSIS

Analyte name	Detections 601 samples	Low (ppb)	High (ppb)	LOQ (ppb)	Avg. % Rec.	Detection Method
Nonachlor, cis isomer	2	1	1.1	1	98	GC/MS-NCI
Nonachlor, trans isomer	2	1.9	3.1	1	96	GC/MS-NCI
Oxadiazon	4	2.3	10.4	2	102	GC/MS-NCI
Parathion ethyl	1	2.3	2.3	2	122	GC/MS-NCI
Pendimethalin	7	2.1	13.4	2	110	GC/MS-NCI
Pentachloroaniline (PCA)	9	1	8.3	1	87	GC/MS-NCI
Piperonyl Butoxide	2	12.6	83.6	8	86	GC/MS-EI
Pirimiphos methyl	1	18.2	18.2	3	43	GC/MS-EI
Prallethrin	1	2.5	2.5	2	116	GC/MS-NCI
Propargite	2	32.8	198	10	72	GC/MS-EI
Propetamphos	1	11.3	11.3	10	103	GC/MS-EI
Quinoxifen	1	5.7	5.7	1	58	GC/MS-EI
Toxaphene [sum]	42	50	748	50	93	GC/MS-NCI
Trifluralin	5	1.4	80.5	1	129	GC/MS-NCI

Summary of Results – April 2008 – April 2010

- 1345 total samples tested
- 2707 pesticide residue detections
- 1637 or 60.5% of the detections came from the DDT family
- Largest Detection = 11.6 ppm of Diflubenzuron
- Residues detected ≥ 100 :
 - Bifenthrin [179]
 - DDT + metabolites [1637]
 - Diphenylamine (DPA) [143]
 - Toxaphene [108]





Thank you for
your attention.