

**“ASSESSING THE OCCURRENCE, DISSIPATION AND POTENTIAL RISKS OF
GLYPHOSATE APPLICATIONS TO NEAR-COASTAL AQUATIC ENVIRONMENTS
WITHIN BISCAYNE NATIONAL PARK”**

GRANT 205000594

PROGRESS REPORT

Submitted to

Biscayne National Park
National Park Service
Department of Interior

By

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July 25, 2005

Assessing the occurrence, dissipation and potential risks of glyphosate applications to near-coastal aquatic environments within Biscayne National Park.

PROGRESS REPORT

July 15, 2005.

Summary of Activities

Because of the heavy use of glyphosate formulations to control unwanted vegetation along canals and structures in South Miami-Dade County resources in areas of Biscayne National Park adjacent to the water control structures could be at risk due to the presence of the active ingredient or the surfactants used in commercial formulations. For that reason, the main purpose of the initial phase of the project was to conduct a detailed survey of canals and coastal environments where glyphosate is applied as vegetation control herbicide concentrating in the following objectives:

- a) Occurrence of the parent herbicide and metabolites
- b) Spatial and temporal distributions
- c) Potential accumulation into marine and limnetic sediments

The original SOW was modified to reflect changes in funding so that only 1/3 of the proposed work will be conducted on the initial phase (Year 1) with the remaining 2/3's to be conducted in the second funding cycle. In addition, at the request of the Park Leader a comprehensive survey of other contaminants such as pesticides and herbicides was required as part of an initial baseline assessment of the study area.

The project award date was DEC31, 2004 but the effective start date was JAN23, 2005. The PI hired the appropriate personnel and ordered the required materials for the glyphosate analysis by FEB25, 2005. Because of the nature of some of the labeled materials and FMOC derivatives they were not available until MAY12, 2005.

A review of the study area was conducted on MAR7 to MAR10, 2005 to select the potential areas for sample collection. The original proposal called for three areas to sample: 1) a typical canal system, 2) an isolated wetland/marsh not influenced by water management activities and 3) a wetland/marsh or basin currently used as part of a water delivery enhancement project. However, the initial selection was based on the locations where vegetation management will be conducted more intensively during 2005. The team surveyed the areas north from Biscayne National Park along the L-31E Canal between the C-102 and C-103 canals and decided to include these three canal systems and their structures in the initial assessments

The team contacted three agencies that could be involved in the control of unwanted vegetation in the study area; Miami-Dade County Public Works, Miami-Dade County Department of Environmental Resource Management and the South Florida Water Management District (Miami and Homestead Offices). The entity responsible for applications of Roundup in South Miami-Dade County canals is the Homestead Office of the SFWMD. The Professional Supervisor, Mr. William Mathis (305-242-5933 x7012) and the Crew Chief Mr. James Sneckenberg (305-242-5933 x7022) provided a schedule of the applications in the study area. Arrangements were made between the FIU team and the SFWMD Homestead office to contact the sampling team prior to the scheduled applications. Based on their tentative schedule (which depends heavily on the rain patterns and weather conditions) an agreement was made to sample the C-102 and C-103 canals during the summer of 2005 since they are treated multiple times between May and September. The L-31E canal however is only treated once a year and a final schedule was not available till the time of this report.

Because of the delays in the scheduled applications the team collected only background assessment samples on APR25, 2005 at four locations along C-102, C-103 and L-31E canals. These samples were analyzed for chlorinated pesticides, PCBs, triazine herbicides, phenoxy acid herbicides, and glyphosate. Only the first three screening methods have been completed to date (Appendix A) and the results for the phenoxy acid herbicides and glyphosate are still pending final QC review.

The preliminary results indicate that Atrazine is present in all the water samples at concentrations ranging from 4.00 to 17.2 ng/L. Since Atrazine is an ubiquitous contaminant in surface waters near urban and agricultural lands these levels were expected. Of all chlorinated compounds analyzed only Endosulfan II was detected in the C-102 sample above the MDL. Once again, at 24.4 ng/L the concentration of this pesticide is well within the levels expected for an area where agrochemicals are still actively used in particular around South Miami-Dade County.

The first sampling during application was conducted at C-102 on MAY24, 2005 and lasted for approximately 8 hours. The FIU crew collected waters along a 100 meter stretch before the application; followed the SFWMD crew and collected multiple samples at the canal banks during the spraying; and returned back to collect waters at the same locations after 3 hours. Although Roundup was being applied to the canal banks we will often see a good portion of the spray reaching the canal waters. All these samples have been extracted for glyphosate and AMPA and are waiting for data reduction and reporting.

The next scheduled sampling will be along C-103 and includes collection of both waters and sediments for a period of 24 hours.

Challenges and limitations.

One of the biggest problems with the project relies on the intermittent scheduling for the applications. Numerous trips have been cancelled because of poor weather conditions such as excessive rainfall and strong winds. In addition, the schedule for the canals in the proposed study area is less frequent than we have estimated thus forcing to conduct more intensive collections at fewer places or have longer waits between collections. It is important to note that L-31E was a key element to assess the transport to wetlands and will be sampled late in the season. FIU has put together fast response sampling kits that will allow the team to collect with very short notice to accommodate to the SFWMD schedules. In addition, the collection crew

will be expanded from two to four people to cover larger areas during the applications, in particular along structures near Biscayne Bay.

Plans for next quarter

The objectives for the best quarter include sampling of C-103 in August and the completion of all the pending analyses. In addition, the team plans to sample sediments from all three canals and the wetlands and tidal creeks east of L-31E to establish the presence/absence of glyphosate, AMPA, and the formulation's inert ingredients.

Sampling along C-102 and L-31N will be conducted when application resumes.

APPENDIX A
ANALYTICAL RESULTS

Biscayne National Park - Triazine Herbicide Monitoring

April 2005

Client Sample ID	BNP	BNP	BNP	BNP
Sample Descriptor	C-102	C-103	L31EA	L31EB
Original Sample				
FIU ID	W3795	W3796	W3797	W3798
Sample Type	Surface Water	Surface Water	Surface Water	Surface Water
SDG	0504D	0504D	0504D	0504D
Sample Volume	1.00	1.00	1.00	1.00
Sample Size Units	Liters	Liters	Liters	Liters
Matrix	Water	Water	Water	Water
Reporting Units	ng/L	ng/L	ng/L	ng/L
Calculation Basis (dry/wet)	Filtered/Wet	Filtered/Wet	Filtered/Wet	Filtered/Wet
QC Batch ID	M0558	M0558	M0558	M0558
Method	GC/MS-SIM	GC/MS-SIM	GC/MS-SIM	GC/MS-SIM
Collection Date	4/25/2005	4/25/2005	4/25/2005	4/25/2005
Receive Date	4/25/2005	4/25/2005	4/25/2005	4/25/2005
Extraction Date	5/2/2005	5/2/2005	5/2/2005	5/2/2005
Analysis Date	5/23/2005	5/23/2005	5/23/2005	5/23/2005
Surrogate Compounds	%Recovery	%Recovery	%Recovery	%Recovery
Atrazine-d5	93	98	91	96
Parent Compounds	Concentration	Concentration	Concentration	Concentration
ATRATON	ND	ND	ND	ND
SIMAZINE	ND	ND	ND	ND
PROMETON	ND	ND	ND	ND
ATRAZINE	4.00	11.0	17.2	16.9
PROPAZINE	ND	ND	ND	ND
TERBUTHYLAZINE	ND	ND	ND	ND
SIMETRYNE	ND	ND	ND	ND
AMETRYNE	ND	ND	ND	ND
PROMETRYNE	ND	ND	ND	ND
TERBUTRYNE	ND	ND	ND	ND

ND Not Detected
 J <MDL
 NA Not Applicable
 Q Results Outside QC
 I Interference
 B Blank Contamination >3xMDL
 D Dilution
 EC Exceeds Calibration

Biscayne National Park - Triazine Herbicide Monitoring

April 2005

Client Sample ID	BLANK	LBS
Sample Descriptor	BLANK	LBS
Original Sample		
FIU ID	Q2093	Q2094
Sample Type	Surface Water	Surface Water
SDG	0504D	0504D
Sample Volume	1.00	1.00
Sample Size Units	Liters	Liters
Matrix	Water	Water
Reporting Units	ng/L	ng/L
Calculation Basis (dry/wet)	Filtered/Wet	Filtered/Wet
QC Batch ID	M0558	M0558
Method	GC/MS-SIM	GC/MS-SIM
Collection Date	N/A	N/A
Receive Date	N/A	N/A
Extraction Date	5/2/2005	5/2/2005
Analysis Date	5/23/2005	5/23/2005
Surrogate Compounds	% Recovery	% Recovery
Atrazine-d5	87	99
Parent Compounds	Concentration	% Recovery
ATRATONE	ND	66
SIMAZINE	ND	86
PROMETON	ND	77
ATRAZINE	ND	86
PROPAZINE	ND	90
TERBUTHYLAZINE	ND	85
SIMETRYNE	ND	71
AMETRYNE	ND	86
PROMETRYNE	ND	80
TERBUTRYNE	ND	71
Average %Recovery		80

ND Not Detected
 J <MDL
 NA Not Applicable
 Q Results Outside QC
 I Interference
 B Blank Contamination >3xMDL
 D Dilution
 EC Exceeds Calibration

Biscayne National Park - Organochlorine Monitoring

April 2005

Client Sample ID	BNP	BNP	BNP	BNP
Sample Descriptor	C102	C103	L31E-A	L31E-B
Original Sample				
FIU ID	W3778	W3779	W3780	W3781
SDG	0504D	0504D	0504D	0504D
Sample Volume	1.00	1.00	1.00	1.00
Sample Size Units	Liters	Liters	Liters	Liters
Matrix	Water	Water	Water	Water
Reporting Units	ng/L	ng/L	ng/L	ng/L
Calculation Basis (dry/wet)	Filtered/Wet	Filtered/Wet	Filtered/Wet	Filtered/Wet
QC Batch ID	M0556	M0556	M0556	M0556
Method	GCECD	GCECD	GCECD	GCECD
Collection Date	04/25/05	04/25/05	04/25/05	04/25/05
Receive Date	04/25/05	04/25/05	04/25/05	04/25/05
Extraction Date	05/02/05	05/02/05	05/02/05	05/02/05
Analysis Date	05/18/05	05/18/05	05/18/05	05/18/05
Surrogate Compounds	%Recovery	%Recovery	%Recovery	%Recovery
DBOFB	90	94	96	99
PCB103	77	89	81	95
PCB198	61	86	90	98
Totals	Concentration	Concentration	Concentration	Concentration
Total HCHs				
Total Chlordanes				
Total DDTs				
Total PCBs				
Total PCBs (S&T)				
Pesticides	Concentration	Concentration	Concentration	Concentration
Chlorinated Benzenes				
Tetrachlorobenzene 1,2,4,5	ND	ND	ND	ND
Tetrachlorobenzene 1,2,3,4	ND	ND	ND	ND
Pentachlorobenzene	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND
Hexachlorocyclohexanes				
Alpha HCH	ND	ND	ND	ND
Beta HCH	ND	ND	ND	ND
Gamma HCH	ND	ND	ND	ND
Delta HCH	ND	ND	ND	ND
Chlorodane-related Compounds				
Heptachlor	ND	ND	ND	ND
Heptachlor Epoxide/OCS	ND	ND	ND	ND
Alpha Chlordane	ND	ND	ND	ND
Gamma Chlordane	ND	ND	ND	ND
Other Cyclodiene Pesticides				
Aldrin	ND	ND	ND	ND
Dieldrin	ND	ND	ND	ND
Endrin	ND	ND	ND	ND
Other Chlorinated Pesticides				
Chlorpyrifos	3.07	J	ND	ND
Mirex		ND	ND	ND
Endosulfan sulfate		ND	ND	ND
Endosulfan II	24.4		ND	ND
DDTs and Related Compounds				
2,4' DDE/ENDOSULFAN I		ND	ND	ND
4,4' DDE		ND	ND	ND
2,4' DDD		ND	ND	ND
4,4' DDD		ND	ND	ND
2,4' DDT		ND	ND	ND
4,4' DDT		ND	ND	ND

ND Not Detected
 J <MDL
 NA Not Applicable
 Q Results Outside QC
 I Interference
 B Blank Contamination >3σMDL
 D Dilution
 EC Exceeds Calibration
 C GC-MS Confirmation

Biscayne National Park - Organochlorine Monitoring April 2005

Client Sample ID	BNP	BNP	BNP	BNP
Sample Descriptor	C102	C103	L31E-A	L31E-B
Original Sample				
FTU ID	W3778	W3779	W3780	W3781
SDG	0504D	0504D	0504D	0504D

Individual PCBs	Concentration	Concentration	Concentration	Concentration
PCB8/5	ND	ND	ND	ND
PCB18/17	ND	ND	ND	ND
PCB29	ND	ND	ND	ND
PCB28/31	ND	ND	ND	ND
PCB52	ND	ND	ND	ND
PCB44	ND	ND	ND	ND
PCB66/95	ND	ND	ND	ND
PCB101/90	ND	ND	ND	ND
PCB87/115	ND	ND	ND	ND
PCB153/132	ND	ND	ND	ND
PCB105	ND	ND	ND	ND
PCB138 /160	ND	ND	ND	ND
PCB187	ND	ND	ND	ND
PCB180	ND	ND	ND	ND
PCB170/190	ND	ND	ND	ND
PCB195/208	ND	ND	ND	ND
PCB206	ND	ND	ND	ND
PCB209	ND	ND	ND	ND

ND Not Detected
 J <MDL
 NA Not Applicable
 Q Results Outside QC
 I Interference
 B Blank Contamination >3xMDL
 D Dilution
 EC Exceeds Calibration
 C GC-MS Confirmation

Biscayne National Park - Organochlorine Monitoring

April 2005

Client Sample ID	BLANK	LBS
Sample Descriptor	BLANK	LBS
Original Sample		
FIU ID	Q2089	Q2090
Sample Type	BLANK	LBS
SDG		
Dry Weight	1.00	1.00
Sample Size Units	Liters	Liters
Matrix	Water	Water
Reporting Units	ng/L	ng/L
Calculation Basis (dry/wet)	Filtered/Wet	Filtered/Wet
QC Batch ID	M0556	M0556
Method	GCECD	GCECD
Collection Date	N/A	N/A
Receive Date	N/A	N/A
Extraction Date	05/02/05	05/02/05
Analysis Date	05/17/05	05/17/05
Surrogate Compounds	%Recovery	%Recovery
DBOFB	91	84
PCB103	94	91
PCB198	83	139
Totals	Concentration	Concentration
Total HCHs	NA	NA
Total Chlordanes	NA	NA
Total DDTs	NA	NA
Total PCBs	NA	NA
Total PCBs (S&T)	NA	NA
Pesticides	Concentration	% Recovery
Chlorinated Benzenes		
Tetrachlorobenzene 1,2,4,5	ND	84
Tetrachlorobenzene 1,2,3,4	ND	87
Pentachlorobenzene	ND	89
Hexachlorobenzene	ND	90
Hexachlorocyclohexanes		
Alpha HCH	ND	90
Beta HCH	ND	92
Gamma HCH	ND	93
Delta HCH	ND	39
Chlordane-related Compounds		Q
Heptachlor	ND	84
Heptachlor Epoxide/OCS	ND	91
Alpha Chlordane	ND	96
Gamma Chlordane	ND	96
Other Cyclodiene Pesticides		
Aldrin	ND	89
Dieldrin	ND	92
Endrin	ND	85
Other Chlorinated Pesticides		
Chlorpyrifos	ND	74
Mirex	ND	97
Endosulfan sulfate	ND	102
Endosulfan II	ND	83
DDTs and Related Compounds		
2,4' DDE/ENDOSULFAN I	ND	92
4,4' DDE	ND	94
2,4' DDD	ND	92
4,4' DDD	ND	97
2,4' DDT	ND	83
4,4' DDT	ND	95

ND Not Detected
 J <MDL
 NA Not Applicable
 Q Results Outside QC
 I Interference
 B Blank Contamination >3xMDL
 D Dilution
 EC Exceeds Calibration

Biscayne National Park - Organochlorine Monitoring

April 2005

Client Sample ID	BLANK	LBS
Sample Descriptor	BLANK	LBS
Original Sample		
FIU ID	Q2089	Q2090
Sample Type	BLANK	LBS
SDG		

Individual PCBs	Concentration	% Recovery	
PCB8/5	ND	97	
PCB18/17	ND	92	
PCB29	ND	91	
PCB28/31	ND	46	Q
PCB52	ND	95	
PCB44	ND	93	
PCB66/95	ND	94	
PCB101/90	ND	95	
PCB87/115	ND	91	
PCB153/132	ND	95	
PCB105	ND	95	
PCB138 /160	ND	97	
PCB187	ND	94	
PCB180	ND	91	
PCB170/190	ND	55	
PCB195/208	ND	90	
PCB206	ND	87	
PCB209	ND	89	

Average Recovery	%	88
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ND Not Detected
 J <MDL
 NA Not Applicable
 Q Results Outside QC
 I Interference
 B Blank Contamination >3xMDL
 D Dilution
 EC Exceeds Calibration